THE SYNTHESIS OF HIGHLY POLAR POLYSTYRENE

By

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"Plans fail for lack of counsel,
but with many advisors they succeed."

Proverbs 15:22

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TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS iii

ABSTRACT vi

CHAPTERS

1 INTRODUCTION 1

2 EXPERIMENTAL 10

General Information 10
An Introduction to High Vacuum Techniques 11
Synthesis of 8-Chloro-3,5-dioxa-4-methyloctane 12
Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane 13
Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane Using 99.9%Li 0.1%Na Wire 13
Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane Using 99%Li 1%Na Wire 14
Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane Using 99%Li 1%Na Dispersion 15
Filtration of 3,5-Dioxa-8-lithio-4-methyloctane Product Mixture 17
Determination of Alkyllithium Initiator Concentration 17
Synthesis of Polystyrene Telechelomer and Polystyrene Carboxylic Acid Using High Vacuum Techniques 18
High Vacuum Method 1 (HV1) 19
High Vacuum Method 2 (HV2) 23
High Vacuum Method 3 (HV3) 24
Synthesis of Polystyrene Telechelomer and Polystyrene Carboxylic Acid under an Argon Atmosphere 29
Argon Method 1 (Ar1) 30
Argon Method 2 (Ar2) 32
Argon Method 3 (Ar3) 32
Argon Method 4 (Ar4) 35
Purification of the Polystyrene-10-Telechelomer 35
Procedure for Polystyrene-10-Telechelomer Precipitation 35
Procedure for Complete Removal of the Acetal Protecting Groups 36
Procedure for Column Chromatography on Polystyrene-10-Telechelomer 37

Procedure for Freeze Drying 39
Synthesis of the Polystyrene-10-Telechelomer Methyl Ester 39
Characterization Methods 40
Molecular Weight Analyses by Titration 40
Minimum Detection of the Acetal Functionality by Proton Nuclear Magnetic Resonance 41
Quantitative Carbon-13 Nuclear Magnetic Resonance Molecular Weight Determinations 41
Molecular Weight Analyses by Vapor Phase Osmometry (VPO) 43
Synthesis of Highly Polar Polystyrene 45
Method 1 (M1) 45
Method 2 (M2) 46
Investigation of Solution Polycondensation Techniques using Tropic Acid 47
Triphenylphosphine and Hexachloroethane Activation 47
Triphenylphosphine Dichloride Activation 48
Dialkylcarbodiimide Activation 49

3 SYNTHESIS OF THE POLYSTYRENE TELECHELOMER 54

Factors Affecting Telechelomer Synthesis 55
Strategy for the Synthesis of a Polystyrene Telechelomer 58
Acetal Initiators 60
The Importance of Lewis Bases 62
Endgroup Carboxylation Using Carbon Dioxide 68
Implementation of the Telechelomer Synthetic Strategy 71
Preparation of 3,5-dioxa-8-lithio-4-methyloctane, Acetal Initiator 71
Anionic Oligomerization of Styrene 72
Termination with Carbon Dioxide 79
Hydrolysis of the Acetal Polystyrene Telechelomer Precursor 82

4 THE FORMATION OF HIGHLY POLAR POLYSTYRENE FROM POLYSTYRENE-10-TELECHELOMER 93

Factors Affecting High and Low Temperature Polycondensation 94
The Synthesis of Highly Polar Polystyrene 104
A "Model" Polymerization Using Tropic Acid 108

REFERENCES 118

BIOGRAPHICAL SKETCH 125

Abstract of Dissertation Presented to the Graduate School
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SYNTHESIS OF HIGHLY POLAR POLYSTYRENE

By

Jeffrey Gerard Linert

DECEMBER 1991

Chairman: Dr. Kenneth B. Wagener
Major Department: Chemistry

A synthesis of polystyrene with regularly occurring ester groups in the backbone (approximately every ten repeat units) has been devised in order to investigate, in the future, the effect of the ester groups on the physical properties of polystyrene. This polar version of polystyrene is formed by high temperature (200+°C) melt polycondensation of polystyrene-10-telechelomer containing a carboxylic acid endgroup and a hydroxyl endgroup.

Polystyrene-10-telechelomer is produced by anionic polymerization using an acetal functionalized alkyllithium (3,5-dioxa-8-lithio-4-methyloctane) to initiate styrene propagation followed by the addition of carbon dioxide to terminate the chains. The Lewis bases, tetrahydrofuran (THF) or N,N,N',N'-tetramethylethylenediamine (TMEDA), are added before or

during initiation to increase the reactivity of the initiator and to provide polymerization systems where the molecular weight of the telechelomer is dictated by the ratio of monomer to initiator concentration. Specifically, using the acetal containing initiator and TMEDA, the target molecular weight of ten repeat units is produced. Tetrahydrofuran activation, however, produces higher than expected molecular weights. In addition, the reactivity of the acetal functionalized initiator is compared to n-butyllithium and is found to be a slower initiator than n-butyllithium.

The termination reaction with carbon dioxide produces 98% carboxylation when TMEDA is used as the only additive; substantially lower carboxylation yields are achieved using THF to activate the initiator. This observation is due to THF ring opening termination reactions. After carboxylation, the acetal endgroup is removed by hydrolysis to form the polystyrene telechelomer.

Low temperature polycondensation of these telechelomers is examined using tropic acid as a model compound; the investigation shows that polymerizations using the activators 1,3-dicyclohexylcarbodiimide (DCC) or 1,3-diisopropylcarbodiimide produce higher molecular weight poly(tropic acid) than do the activators triphenylphosphine-hexachloroethane or triphenylphosphine dichloride. The molecular weight of the polymer produced in the dialkylcarbodiimide systems increases with decreasing polymerization temperature (-20°C>0°C>25°C) and with decreasing solvent polarity (cyclohexane/THF[5:2 by volume]>toluene/THF[5:2]>dichloromethane). In addition, higher molecular weight poly(tropic acid) is produced with 0.5 equivalents of the catalysts, p-toluenesulfonic acid and 4-(dimethylamino)pyridine, than with 0.04 equivalents of p-toluenesulfonic acid and 0.35 equivalents of pyridine.

CHAPTER 1
INTRODUCTION

The polystyrene story began in 1839 when Eduard Simonin reported the isolation of styrene (Figure 1.1), then called "styrol," by steam distillation of an extract from the trees of *Liquambar orientalis*.[1] The major component of the extract, cinnamic acid **(1)**, decarboxylated to form styrene during the distillation. After standing for months, the "styrol" was transformed into a "jelly-like material" which 70 years later became known as polystyrene **(2)**.[2]

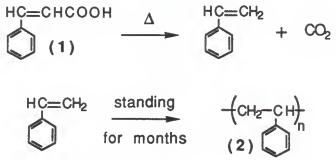


Figure 1.1. The first synthesis of polystyrene.

Polystyrene remained a laboratory curiosity until about 1930 when an economical synthesis of polymerization-grade styrene was developed.[1] Soon afterward, the synthetic rubber program of World War II demanded large quantities of styrene monomer, which forced the chemical industry to increase its production. When the war ended, there was an excess of

high-grade, low-cost styrene, leading to the intensive research which produced numerous applications for polystyrene.[3-10]

One of the most useful properties of polystyrene is its reasonably high glass transition temperature of 100°C.[11] Above this temperature, the polymer chains can rotate independently, and the polymer becomes a processible viscous liquid which, upon cooling, becomes a strong solid.[12,13]

These thermal properties of polystyrene are caused by the bulky phenyl substituents which hinder the movement of the main chain.[14,15,16] The effect of pendant group size is significant, as shown by comparison of the glass transition temperatures of ethylene **(3)**,[17] polypropylene **(4)**,[18] and polystyrene **(2)** (Figure 1.2); the polyethylene chains begin to rotate roughly 100°C before polypropylene and 200°C before polystyrene.[16]

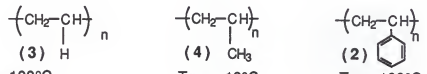


Figure 1.2. Glass transition temperatures of polyethylene **(3)**, polypropylene **(4)**, and polystyrene **(2)**.

The pendant groups of polystyrene also affect the ability of the polymer to crystallize.[19,20] If the stereochemical placement of the phenyl substituents is not regular, as is the case in the majority of the polystyrene made by anionic, free radical, or cationic synthetic techniques,[20] then the polymer is atactic (Figure 1.3a) and does not crystallize. However, isotactic and syndiotactic polystyrene chains

(Figure 1.3b and c), produced by Ziegler-Natta polymerization, can form a crystal lattice.[21,22]

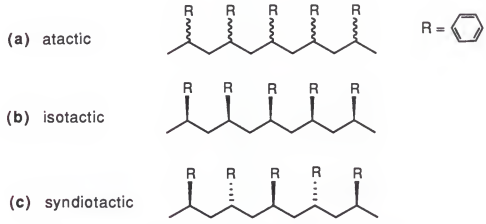


Figure 1.3. Stereochemical isomers of polystyrene.

The crystalline isomers of polystyrene are more solvent-resistant due to the strong interactions between chains. They can be used at higher temperatures since these polystyrene crystals melt between 240°C to 270°C.[20]

Both the solvent resistance and the maximum-use temperature of atactic polystyrene are increased if a percentage (1% to 15%) of the pendant phenyl groups are substituted with sulfonate or carboxylate salts at the para position (Figure 1.4).[23-25]

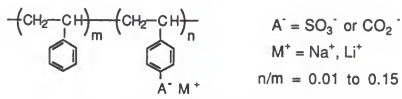


Figure 1.4. Polystyrene functionalized with metal carboxylate or sulfonate salts.

The pendant ionic groups aggregate into clusters which increase the interaction between chains as shown in Figure 1.5.

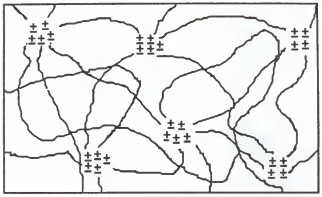
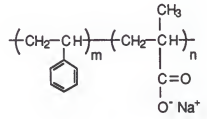


Figure 1.5. Schematic diagram of cluster formation in ion-containing polystyrene.[26]

These so-called "ionomers" possess two glass transition temperatures. The first occurs at a temperature slightly higher than polystyrene homopolymer and is caused by the onset of rotational motion of the polymer chain sections between the clusters (Figure 1.5).[25,27] The polymer chain sections which are closer to the clusters have a glass transition 50°C to 100°C higher than polystyrene homopolymer because the interactions between chains hinder their mobility.[27,28]

Another example of ion-containing polystyrene is the sodium salt of the copolymer of methylacrylic acid and styrene (Figure 1.6).[25,29] In this case, the polar group is closer to the main chain of the polymer than the sulfonated or carboxylated polymers. The ions increase the glass transition temperature and solvent resistance in the same way as the

phenyl substituted ionomers; however, the poly(styrene-co-sodium methacrylate) forms larger aggregates.[27]



n/m = 0.01 to 0.15

Figure 1.6. Poly(styrene-co-sodium methacrylate).

The effects of a polar group inserted into the main chain of polystyrene have not been extensively investigated. In 1982, Bailey published the synthesis of poly[γ-(-ß-phenyl)butyrolactone] (Figure 1.7).[30]

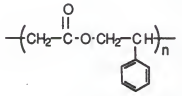


Figure 1.7. Poly[γ-(-ß-phenyl)butyrolactone].

While the structure is interesting, the effects of the polar group on the physical properties of the polymer were not studied. Later, Bailey used free radicals to form copolymers of styrene and 2-methylene-1,3-dioxepane **(5)** in which randomly occurring ester groups seperated polystyrene segments **(6)** (Figure 1.8).[31,32]

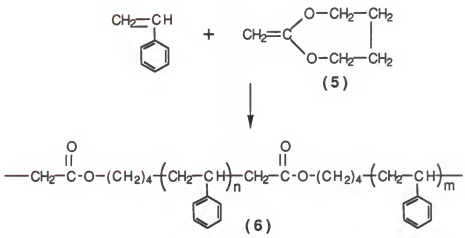


Figure 1.8. Copolymerization of styrene and 2-methylene-1,3-dioxepane (**5**) forms polystyrene with ester group in the main chain (**6**).

These polymers are reported to be more heat resistant and biodegradable than the polystyrene homopolymer.[33]

Regular placement of the ester group in the backbone of polystyrene can be expected to increase the interaction between the chains to a greater extent than the random copolymers synthesized by Bailey. The formation of one diester interaction may facilitate the formation of a neighboring diester interaction as shown in Figure 1.9.[34,35]

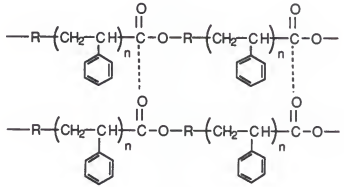


Figure 1.9. Regular placement may enhance interchain interaction.

To this date, the effects of a regularly occurring main-chain polar group on the physical properties of polystyrene have not been investigated, perhaps because there had been no obvious synthetic route to this type of polymer.

The objective of the research discussed herein is to devise a synthetic strategy which creates polystyrene with regularly occurring ester groups in the main chain of the polymer. This synthetic strategy employs chain/step polymerization methodology (Figure 1.10). A polystyrene telechelomer **(7)**, formed by chain polymerization from styrene, is used as a monomer in a step polymerization, which forms highly polar polystyrene **(8)**.

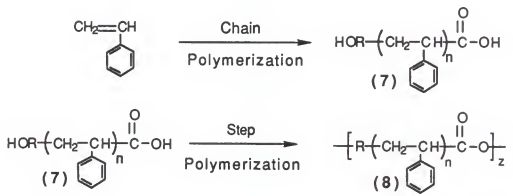


Figure 1.10. The chain/step polymerization strategy used to synthesize highly polar polystyrene **(8)**.

Since the telechelomer chain lengths are nearly equivalent, the telechelomer's polycondensation creates uniform spacing between the ester groups of highly polar polystyrene. Similarly, the length of the ester spacer is controlled by the length of polystyrene telechelomer; as a result, the effect of different spacer lengths on the physical properties of the

modified polystyrene can also be investigated using this synthetic strategy.

The polystyrene telechelomer described in this dissertation has an average chain length of 10 styrene repeat units and is referred to as polystyrene-10-telechelomer **(9)**. The telechelomer synthetic scheme, shown in Figure 1.11, begins with the anionic polymerization of styrene initiated with an alkyllithium initiator **(10)**, resulting in a polystyryllithium anion **(11)** which reacts with carbon dioxide to form a carboxylate salt **(12)**. The polystyrene-10-telechelomer **(9)** is formed upon removal of the protecting group and protonation of the carboxylate anion.

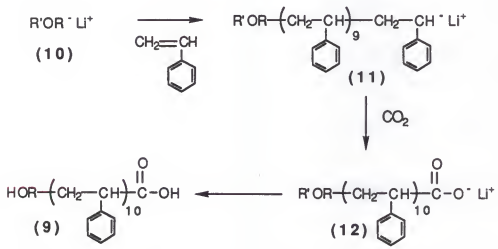


Figure 1.11. Synthetic scheme used to produce the polystyrene-10-telechelomer **(9)**.

The results of this dissertation are presented according to the chain/step methodology used in the synthesis of highly polar polystyrene. Chapter 3 discusses the investigations relating to telechelomer synthesis,

and the investigations of the telechelomer polycondensation are discussed separately in Chapter 4. The procedures used in the synthesis and characterization of the telechelomer and highly polar polystyrene are described in Chapter 2.

CHAPTER 2
EXPERIMENTAL

General Information

All NMR spectra were obtained with either a Varian XL-200 or a Varian VXR-300 Spectrometer. Chemical shifts are reported in parts per million (δ) downfield from the internal reference tetramethylsilane. All spectra were taken in deuterated chloroform. Infrared spectral analysis was performed on a Perkin Elmer 281 or a Perkin Elmer model 1600 FT Spectrophotometer using sodium chloride plates and recording percent transmission relative to wavenumber. Reagent purity was determined on a Hewlett Packard 5880A Series Gas Chromatograph. The SEC instrument used incorporates a Waters 6000A solvent delivery system, an R-401 refractive index (RI) detector, and a Perkin Elmer LC-75 ultraviolet-visible (UV) spectrophotometric detector. Separation was achieved on a set of Phenogel and TSK columns of pore size ranging from 500 to 10^5 Å using tetrahydrofuran as the mobile phase. This instrument was calibrated with polystyrene standards purchased from Scientific Polymer Products (30,000-1000 g/mol) and Pressure Chemical (1500-500 g/mol). Polymer molecular weights and distributions were calculated from experimental data using a method described by Hamielic which includes a correction for band broadening.[36] The polystyrene oligomers were analyzed by thin layer chromatography (TLC) using Kodak #13181 silica gel plates with fluorescent indicator. The plates (7 cm long) were spotted with a 2%-4%

(g/ml) polymer and dichloromethane solution. Elemental analyses were completed by Atlantic Microlab, Norcross, GA (for carbon, hydrogen) or Galbraith Laboratories, Knoxville, TN (for oxygen).

Unless otherwise specified, reagents were obtained from Aldrich Chemical Company. Solvents were purchased from Fisher Scientific and were certified A.C.S. reagent grade. Argon (99+% pure) was purchased from Liquid Air, Inc.

An Introduction to High Vacuum Techniques

High vacuum techniques are effective for highly air-sensitive reactions such as anionic polymerization because reagents and solvents can be purified and transferred with essentially no contamination by atmospheric moisture or oxygen.[37,38]

Purification is accomplished by distillation from an appropriate reagent, and transfers can be made either by distillation or by the use of an ampule. Distillation is accomplished easily by cooling the receiving flask and warming the distilling flask. An ampule is used when reagents must be added all-at-once.

An ampule is calibrated before use, filled with an appropriate amount of reagent by distillation, and sealed under high vacuum. The high vacuum seal is made by melting the sides of the glass tube together using an oxygen-methane torch. Once the glass melts, the walls of the glass tube are drawn together by the vacuum, creating an airtight seal. With continued heating and elongation of the melted seal, the ampule is separated from the vacuum line.

The other side of the ampule is a glass tube which has a breakable seal (a breakseal) and an open end. The open end is attached to the reaction

flask using an oxygen-methane torch. When the reagent is needed, a magnet inside the flask is used to break the breakseal, which causes the reagent to pour into the flask (see Figures 2.2 and 2.3).

Synthesis of 8-Chloro-3,5-dioxa-4-methyloctane

The synthesis employed follows the procedure of Eaton[39] closely. Purification of chloropropanol by extraction with saturated sodium bicarbonate as described by Eaton did not increase the purity of the 98% reagent purchased from the Aldrich Chemical Company. To a solution of chloropropanol (100 g,1.2 mol) and ethyl vinyl ether (180 ml,1.9 mol) was added dichloroacetic acid in three batches (1.70 ml, 20 mmol; 0.61 ml, 7.4 mmol; 0.61 ml, 7.4 mmol) to avoid a large exotherm; the first was added immediately, the second after 1 hour, and the third after 3 hours. After stirring overnight, 5 grams of sodium carbonate were added, and the mixture was stirred an hour, filtered, and rotary evaporated. The product was fractionally distilled (36-38°C) at 6 mmHg. The higher boiling fractions were pure by NMR but low concentrations of alcohol were detected by infrared analysis. The acetal product cannot be analyzed by gas chromatography because of decomposition. Higher purity can be achieved by collecting the higher boiling fractions of another distillation (65-70°C) at 20 mmHg. The product (160 ml, 160 g) was stored until use over sodium carbonate. Extended storage (months) leads to decomposition into chloropropanol and acetaldehyde.

^{1}H NMR (δ): 4.7 (1H, quartet), (3.8-3.3) (6H, multiplet), 2.0 (2H, quintet), 1.3 (3H, doublet), 1.1 (3H, triplet)

^{13}C NMR (δ): 99.6 (O-$\underline{C}H$), 61.3 (O-$\underline{C}H_2$), 60.9 (O-$\underline{C}H_2$-CH_3), 41.8 ($\underline{C}H_2$-Cl), 32.1(CH_2), 19.7 ($\underline{C}H_3$-CH), 15.2 ($\underline{C}H_3$)

IR (cm^{-1}): 3000 (s, C-H stretch), 1190-1380 (s, C-O-C stretch)

Elemental analysis (%): C-50.62, H-9.10 (found);
C-50.44, H-9.09 (calculated for $C_7H_{15}ClO_2$)

Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane

Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane Using 99.9%Li 0.1%Na Wire

This procedure, which was adapted from Eaton,[39] used high vacuum techniques. The reaction flask was a modified 250 ml round bottom flask equipped with an ampule of 8-chloro-3,5-dioxa-4-methyloctane (5.2 ml, 31 mmol, distilled from calcium hydride) and an open-ended glass tube through which lithium wire was added against a stream of argon. The lithium wire had been washed with hexane, scraped with a spatula, cut into 1 cm lengths, submerged in methanol, and resubmerged in hexane. After the lithium was added, the sidearm was capped with a septum, and the system was evacuated to 10^{-3} mmHg pressure. The tube through which the lithium was added was sealed with an oxygen-methane torch. The diethyl ether was distilled into the flask under high vacuum ($1x10^{-5}$ mmHg). The ampule containing 8-chloro-3,5-dioxa-4-methyloctane was broken, and the reaction was allowed to stir 12 hours at room temperature. Then a sample of the product was neutralized with water, dried with magnesium sulfate, filtered, and analyzed spectroscopically; the analyses showed predominantly unreacted starting material along with a low concentration of 3,5-dioxa-4-methyloctane.

^{1}H NMR (δ) (integral): 4.7 (CH, 9.84), 4.0 (1.30), 3.8-3.4 (0-CH_3, 72.0), 2.0 (CH_2-Cl, 16.7), 1.55 (CH_2-CH_2-CH_3,1.3), 1.1-1.3 (CH_3, 74.9), 1.0-0.8 (CH_2-CH_2-CH_3,1.7)

^{13}C NMR (δ): 99.6 (O-CH), 99.2 (O-CH), 67 (O-CH_2-CH_2), 66 (ether), 61.3 (O-CH_2), 60.9 (O-CH_2), 60.5 (O-CH_2), 41.8 (CH_2-Cl), 32.7 (CH_2-CH_2-Cl), 23 (CH_2-CH_2-CH_3), 19.7 (CH-CH_3), 15.2 (ether), 10.9 (CH_2-CH_3)

Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane Using 99%Li 1%Na Wire

The 8-chloro-3,5-dioxa-4-methyloctane (11.5 ml, 69.7 mmol) used in this procedure was distilled from calcium hydride at 1 mmHg into a flame dried Schlenk tube, and the tube backfilled with argon. All glassware was dried in a 100°C oven overnight and assembled hot. The reaction flask was a three neck flask, equipped with an argon inlet, a magnetic stirbar, a constant addition funnel, and a bend arm adaptor which held a Schlenk tube used as the argon outlet. The system was flame dried three times while an argon stream was moving through the flask; the argon inlet was moved to the top of the constant addition funnel so that it could also be flame dried. Lithium (1%) sodium wire (174 mmol, 27 cm) was loaded into the flask in the following way: The argon flow was increased, and the constant addition funnel was taken off and attached to another flask temporarily. A length of lithium wire (1 cm) was cut from the roll, washed in hexane, flattened with a hammer on a stainless steel plate, sliced with scissors and allowed to fall directly into the flask; then the opening of the flask was stoppered with a septum. The process was repeated as quickly as possible 26 times. The constant addition funnel was returned to the three neck flask and diethyl either, distilled from sodium under argon, was

syringed onto the lithium via a septum at the top of the funnel. Then 8-chloro-3,5-dioxa-4-methyloctane was syringed into the funnel, and one milliliter was added to the diethyl ether-lithium mixture. When the solution turned cloudy (10 min.), the flask was placed in a -5°C to -10°C bath, and the remaining 8-chloro-3,5-dioxa-4-methyloctane was added slowly over 45 minutes. After three hours, the white solution was poured into a Schlenk tube via the bend arm adaptor by tipping the flask, and the Schlenk tube was quickly removed and stoppered. The product was stored at -30°C in a desiccator. Concentration was determined by a fluorine titration method described below. Yield is 60 ml of a 0.86M solution, or 74%.

Synthesis of 3,5-Dioxa-8-lithio-4-methyloctane Using 99%Li 1%Na Dispersion

The 8-chloro-3,5-dioxa-4-methyloctane (0.21 mol, 35 ml) was distilled from calcium hydride at 1 mmHg into a flame-dried Schlenk tube, and the flask backfilled with argon. The left neck of the three-neck flask used in this procedure was replaced with a course-glass frit topped with a male ground-glass joint which held a Schlenk tube used as the argon outlet. Another Schlenk tube was attached to the right neck of the flask via a bent arm adaptor and this Schlenk tube also served as the argon inlet. In addition, the flask was equipped with a magnetic stirbar and a constant addition funnel. All glassware was dried overnight in a 100°C oven, assembled hot, and flame dried three times while an argon stream was moving through the flask. The argon outlet was moved to the top of the constant addition funnel so it could also be flame dried.

The lithium dispersion 30% packaged in mineral oil (purchased from Aesar) is solid at room temperature; consequently, the dispersion was heated until it flowed by placing the bottle in a 100°C oil bath for 30 minutes. The bottle was then weighed quickly, the argon flow increased, the constant addition funnel removed, the lithium dispersion in mineral oil poured into the flask, and the constant addition funnel replaced. The bottle containing the dispersion was reweighed so that the amount of lithium used would be known (0.65 mol, 15 g). The mineral oil was removed by adding hexane, freshly distilled from sodium and potassium alloy, onto the dispersion and filtering the hexane through the glass frit into the left-hand Schlenk tube, which was quickly removed, emptied, and replaced. The dispersion was washed with hexane by this process three times.

The constant addition funnel was then returned to the three-neck flask and diethyl either, distilled from sodium under argon, was syringed onto the lithium through a septum at the top of the funnel. The 8-chloro-3,5-dioxa-4-methyloctane was syringed into the funnel, and one milliliter was added to the diethyl ether lithium mixture. When the solution turned cloudy (10 min.), the flask was placed in a -5°C to -10°C bath, and the remaining acetal was added slowly over 45 minutes. After three hours, the white solution was poured into a Schlenk tube via the bent arm adaptor by tipping the flask, and then the Schlenk tube was quickly stoppered. The product was stored at -30°C in a desiccator. Later, the solution was filtered through a glass wool plug as described in the section titled "Filtration of 3,5-Dioxa-8-lithio-4-methyloctane Product Mixture," and alkyllithium concentration was determined by the fluorine titration method described in the section titled "Determination of Alkyllithium Initiator Concentration." Yield is 144 ml of a 1.15 molar solution or 79%.

A few milliliters of the alkyllithium diethyl ether solution was reacted with water, dried with sodium carbonate, and analyzed for loss of starting material by NMR.

^{1}H NMR (δ) : 4.7-4.6 (C<u>H</u>), 3.7-3.3 (O-C<u>H</u>$_2$), 2.25-2.1, 1.70-1.50 (C<u>H</u>$_2$), 1.7-1.1 (C<u>H</u>$_3$), 1.0-0.8 (CH$_2$-CH$_2$-C<u>H</u>$_3$)

^{13}C NMR (δ): 99.6 (<u>C</u>H-O), 67 (O-<u>C</u>H$_2$-CH$_2$), 60.9 (O-<u>C</u>H$_2$), 23 (O-CH$_2$-<u>C</u>H$_2$), 19.7 (CH-CH$_3$), 15.2 (CH$_2$-<u>C</u>H$_3$), 10.9 (CH$_2$-<u>C</u>H$_3$)

<u>Filtration of 3,5-Dioxa-8-lithio-4-methyloctane Product Mixture</u>

The 3,5-dioxa-8-lithio-4-methyloctane solution in a Schlenk tube was poured, using a bent arm adapter, through a vacuum adapter, which contained a plug of glass wool, into another Schlenk tube. A slight vacuum was applied below the plug, and an argon pressure was applied above the plug.

CAUTION: The lithium dispersion and lithium chloride mixture which is separated by the filtration is a flammable solid which may ignite upon exposure to air. The solid should be immediately submersed in hexane and destroyed with small portions of methanol.

<u>Determination of Alkyllithium Initiator Concentration</u>

Flourene (0.402 g, 2.42 mmol) was loaded into a flame-dried Schlenk tube, and the system was evacuated and purged with argon three times. Tetrahydrofuran (10 ml), distilled from sodium and potassium alloy, was syringed through a septum, and the solution was immersed in a -78°C bath for 5 to 10 minutes. Then the alkyllithium solution (2 ml) was added, and the contents swirled in the -78°C bath for 5 minutes. The orange solution was allowed to warm to room temperature for 15 minutes and then methyl

iodine, distilled from calcium hydride and stored under argon in a desiccator at -30°C, was added. The ratio of fluorine to 9-methylfluorine, determined by gas chromatography, is proportional to the concentration of alkyllithium in solution. The formulas shown in Figure 2.1 were used to determine the concentration of alkyllithium.

Fraction of 9-methylfluorene:

$$\frac{\text{(Area of 9-methylflourene/13)}}{\text{(Area of fluorene/12) + (Area of 9-methylflourene/13)}}$$

Concentration of solution:

$$\frac{\text{(Fraction of 9-methylfluorene) x (initial moles of fluorene)}}{\text{(liters of alkyllithium solution used)}}$$

Figure 2.1. Formulas used to determine alkyllithium concentration.

The method produced results consistent with the Gilman double titration technique. A n-butyllithium solution was analyzed twice by the fluorene method and the Gilman technique;[40,41] the average concentration values 1.519 M (fluorene) and 1.527 M (Gilman) agree within 2%.

Synthesis of Polystyrene Telechelomer and Polystyrene Carboxylic Acid Using High Vacuum Techniques

Benzene and toluene were extracted with sulfuric acid as described by Perrin.[42] The solvents benzene, toluene and THF were dried with calcium hydride and distilled onto sodium and potassium alloy. Tetrahydrofuran was stored over the alloy, but benzene and toluene were distilled from the alloy and stored in the presence of polystyryllithium (used in low concentration primarily as an indicator of solvent purity).

Styrene was fractionally distilled from calcium hydride under a 1 mmHg vacuum and redistilled under high vacuum calcium hydride into ampules. In some cases, the styrene was purified with dibutylmagnesium (2 mole% compared to styrene). The magnesium compound, purchased in hexane from Alfa Chemicals, was transferred into a flask via cannula or syringe. The flask was evacuated; the hexane was removed, and the styrene was distilled into the flask. After at least an hour, the styrene was distilled into ampules.

Carbon dioxide (99.999% purity) was purchased from Airco Specialty Gases. The tank was attached to the vacuum line using Cajon Ultratorr fittings and flexible stainless steel tubing. Argon was attached to the vacuum line via Tygon tubing equipped with a bubbler.

A single stage diffusion pump filled with Dow Corning diffusion pump fluid was used for the first 2 high vacuum methods. The manifold employed contained 5 three-way glass stopcocks. Solvent (benzene and THF) stills were attached to the line via ground-glass joints.

High Vacuum Method 1 (HV1)

TMEDA used in this experiment was distilled once from calcium hydride into ampules. Styrene was additionally distilled from dibutylmagnesium before distillation into ampules. Both the polystyrene telechelomer and the polystyrene carboxylic acid were synthesized by this method. The experiments were performed such that the only significant difference in the procedures was the type of initiator used--3,5-dioxa-8-lithio-4-methyloctane produced polystyrene telechelomer, and n-butyllithium produced polystyrene carboxylate.

The reaction vessel was a modified 500 ml round bottom flask (RB1) with a 200 ml round bottom (RB2) and a 50 ml round bottom (RB3) attached to it with glass tubing (Figure 2.2). Round bottom one (RB1) was also equipped with a TMEDA ampule (180 mmol), a styrene ampule (290 mmol), and a glass tube through which the initiator could be added. Round bottom two (RB2) was equipped with a TMEDA ampule (20 mmol) and a sidearm with a breakseal, and RB3 was equipped with an ampule of degassed methanol (25 ml).

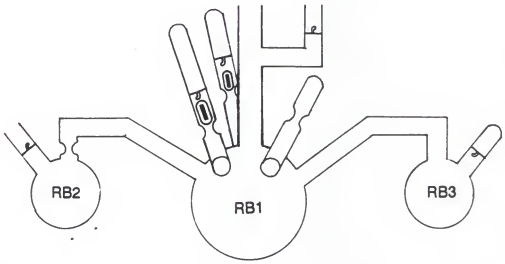


Figure 2.2. Polymerization flask used for high vacuum methods 1 and 2.

The reaction vessel was attached to the vacuum line and evacuated. It was then filled with argon, and a diethyl ether solution of 3,5-dioxa-8-lithio-4-methyloctane (35 mmol, 40 ml) or a hexane solution of n-butyllithium (35 mmol, 20 ml) was added by removing the septum on the open-ended tube and injecting the solution by syringe. After replacing the septum, the flask was cooled to -78°C and evacuated. The open-ended tube was sealed below the septum with an oxygen-methane torch, and benzene

(300 ml) was distilled into the flask, which was sealed and removed from the vacuum line upon completion of the distillation. Then the solution was allowed to thaw, and styrene was added.

After three hours, a portion of the polystyryllithium anion solution (approximately 100 ml, 10 mmol) was poured into RB2, which was then separated from the reaction flask and stored for later use (see High Vacuum Method 2). In a similar way, some of the polystyryllithium solution was poured into RB3, which was then separated from RB1. The polystyryllithium solution in RB3 was neutralized by adding methanol.

The TMEDA ampule on RB1 was then opened and the polystyryllithium solution was swirled. Then the reaction flask (RB1) was reconnected to the vacuum line via the breakseal and carbon dioxide was introduced at slightly over 1 atmosphere pressure.

The reaction solution was then reduced by rotary evaporation and stirred with an excess of HCl dissolved in a small amount of methanol for an hour (the methanol was minimized to avoid precipitation). The polymer was then precipitated into 200 ml to 500 ml of methanol.

Characterization of acetal polystyrene from RB3:

^{1}H NMR (δ): 7.3-6.8 (0.3725), 6.8-6.3 (0.2331), 4.7-4.5 (0.0040), 3.6-3.0 (0.0180), 2.3-0.97 (0.3724) see Figure 3.26.

^{13}C NMR (δ): 146-144, 129-124, 99.6 (O-$\underline{C}$H), 65.0 (O-$\underline{C}$H$_2$-CH$_2$), 60.7 (O-$\underline{C}$H$_2$-CH$_3$), 47.1-38.9, 29.7 (O-CH$_2$-$\underline{C}$H$_2$), 24.3 (O-CH$_2$-CH$_2$-$\underline{C}$H$_2$), 19.7 (CH-$\underline{C}$H$_3$), 15.5 (CH$_2$-$\underline{C}$H$_3$) see Figure 3.28

IR (cm^{-1}): 3000-2900 (s, C-H stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1190-1380 (s, C-O-C)

TLC (Rf): 0.0, 0.8 (dichloromethane)

Characterization of polystyrene telechelomer from RB1:

^{1}H NMR (δ): 7.3-6.8 (0.3725), 6.8-6.3 (0.2331), 4.7-4.5 (0.0040), 3.6-3.0 (0.0180), 2.3-0.97 (0.3724) see Figure 3.26.

^{13}C NMR (δ): 146-144, 129-124, 99.6, 65.0, 60.7, 47.1-38.9, 29.7, 24.3, 19.7, 15.5 see Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1690 (w, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 5200 (SEC), 7540 (titration)

Molecular Weight $\overline{M}_w$: 7500 (SEC)

Carboxylation ($\overline{M}_n$(SEC)/$\overline{M}_n$(titration)) %: 69

TLC (Rf): 0.0, 0.5 (dichloromethane)

Elemental analysis (%): C-89.57, H-7.89 (found); C-91.6, H-7.67 (calculated based on 5200 g/mol and 69% carboxylation)

Characterization of polystyrene carboxylic acid:

^{1}H NMR (δ) (integral): 7.4-6.4, (0.623); 2.6-0.82 (0.368); 0.9-0.7 ($C\underline{H}_3$, 0.009) See Figure 3.26.

^{13}C NMR (δ): 145, 128, 126, 47.1-38.9, 33.0 ($\underline{C}H_2$-CH_2-CH_2-CH_3), 27.0 ($\underline{C}H_2$-CH_2-CH_3), 22.5 ($\underline{C}H_2$-CH_3),14.0 (CH_3) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 2950 (s, C-H stretch), 1600,1490 and 1450 (m, s, s, aromatic stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 3800 (SEC), 4900 (titration)

Molecular Weight $\overline{M}_w$: 4600 (SEC)

Carboxylation ($\overline{M}_n$(SEC)/$\overline{M}_n$(titration)) %: 78

TLC (Rf): 0.1, 0.9 (dichloromethane)

Elemental analysis (%): C-90.66, H-7.87 (found); C-91.8, H-7.54
(calculated based on 3800 g/mol and 78% carboxylation)

High Vacuum Method 2 (HV2)

This procedure uses the portion of the polystyryllithium anion solution which was stored in RB2 (Figure 2.2) as described in the section "High Vacuum Techniques Method 1 (HV1)." The reaction flask labeled RB2 in Figure 2.3 was equipped with a TMEDA ampule (34 mmol) and a breakseal. The TMEDA ampule (34 mmol) was opened, and the solution was swirled and then frozen. Round bottom 2 was reattached to the vacuum line via the breakseal, and the frozen benzene/TMEDA solution was sublimed from the system leaving a porous polystyryllithium anion solid, which was carboxylated instantly upon exposure to carbon dioxide. The solid was then dissolved in dichloromethane and stirred with a methanol-HCl solution.

^{1}H NMR (δ) (integral) : 7.6-6.3, (m, 0.6227), 3.7-3.4 (m, 0.3681), 3.3 (m, 0.0013), 2.6-0.82 (m, 0.3595) see Figure 3.26

^{13}C NMR (δ): 146-144, 129-124, 63.0, 47.1-38.9, 33.0, 23.5 see Figure 3.28

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 5200 (SEC), 6790 (titration)

Molecular Weight $\overline{M}_w$: 6500 (SEC)

Carboxylation ($\overline{M}_n$(SEC)/$\overline{M}_n$(titration))%: 76

TLC (Rf): 0.1, 0.4 (dichloromethane)

Elemental analysis (%): C-90.64, H-7.74 (found); C-91.6, H-7.72
(calculated based on 5200 g/mol and 76% carboxylation)

High Vacuum Method 3 (HV3)

The following four investigations were completed with this method:

Investigation 1 THF added first, TMEDA second

Investigation 2 TMEDA added first, THF second

Investigation 3 TMEDA added first, TMEDA second

Investigation 4 TMEDA added first, TMEDA second

Styrene was additionally distilled from dibutylmagnesium before distillation into ampules, and TMEDA was distilled from calcium hydride and redistilled from sodium dispersion before distillation into ampules. Benzene was distilled from calcium hydride onto sodium dispersion and then stored on the presence of polystyryllithium. Tetrahydrofuran was fractionally distilled from lithium aluminum hydride and redistilled onto sodium and potassium alloy before distillation into ampules.

These experiments used a vacuum line which contains a triple stage diffusion pump and two Welch model 1400 vacuum pumps, one used with the diffusion pump and the other was used as a roughing pump.[37] All stopcocks on this vacuum line are Teflon from Rotoflow or Kontes.[38] An acceptable vacuum was defined by the discharge Tesla coil produced when close to the vacuum line; no sound or color was indicative of high vacuum. Tetrahydrofuran and benzene were stored in round bottom flasks equipped with Teflon stopcocks and ground-glass joints, which allowed the stills to be removed and reattached when needed. After the round bottoms were reattached, the solvent was exposed to vacuum three to six times before distillation into the reaction flask or ampules. After distillation, a full vacuum was applied to the frozen, freshly distilled solvent for 30 minutes.

A polymerization flask equipped with a Rotoflow stopcock and four ampules (Figure 2.3) was attached onto a high vacuum line and flame dried

repeatedly until high vacuum was achieved. After the vacuum was quenched with argon, the Rotoflow plug was removed and replaced with a septum.

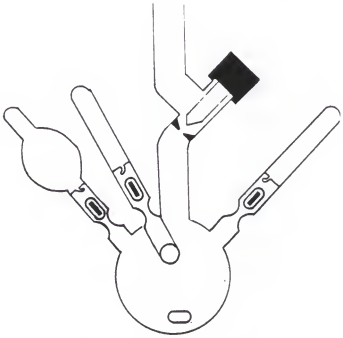


Figure 2.3. Polymerization flask used for high vacuum method 3.

The diethyl ether initiator solution (32 mmol) was syringed through the septum into the polymerization flask. The initiator solution was cooled to -78°C, and the flask was evacuated with a roughing pump. Then the solution was frozen with liquid nitrogen, exposed to high vacuum, and allowed to warm to -78°C for 30 minutes.

Benzene (220 ml) was then distilled into the flask under high vacuum, and a TMEDA (38 mmol) or THF (64 mmol) ampule was ruptured using a glass-enclosed magnetic hammer. When the benzene, initiator, and TMEDA (or THF) solution had reached 25°C and was stirring rapidly, the styrene (320 mmol) ampule was ruptured, creating a deep burgundy solution. After

3 to 4 hours (1 hour if THF was added first), additional TMEDA (640 mmol) or THF (770 mmol) was added, and the system cooled to O°C. Then the magnetic stirrer was stopped, and carbon dioxide was introduced. After 24 hours, the solution was poured into a round bottom flask; the solvents were removed by rotary evaporation, and the product was redissolved in dichloromethane. To this solution, 6M aq. HCl was added; the mixture was stirred for 6 hours and then extracted with water until washings were neutral to pH paper. After the dichloromethane solution was dried with magnesium sulfate and filtered, the solvent was removed by rotary evaporation followed by drying in a vacuum oven overnight at room temperature.

Characterization of telechelomer produced by investigation 1:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.6227), 6.1-5.6 (0.0242), 5.3-5.2 (0.0009), 3.7-3.1 (0.3681), 2.6-1.3 (0.3366) See Figure 3.26.

^{13}C NMR (δ) (integral):178 (0.0034),147-144 (0.108); 130-124 (0.6190), 63.2-62.2 (0.0085), 49.9-48.5 (0.0096), 47.7-39.6 (0.2278), 38.6-32.1 (0.0052), 32.6 (0.0071), 23.5 (0.0077) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 1600 (^{13}C NMR), 1900 (SEC), 1800 (VPO), 2430 (titration)

Molecular Weight $\overline{M}_w$: 2200 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration)) %: 66±10

TLC (Rf): 0.1, 0.5 (dichloromethane)

Elemental analysis (%): C-88.37, H-7.89, O-2.50 (found); C-89.8, H-7.67, O-2.32 (calculated based on 1600 g/mol and 66% carboxylation)

Characterization of telechelomer produced by investigation 2:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5896), 5.63-5.0 (0.0192)), 3.9-3.7 (0.0027), 3.7-3.2 (0.0314), 2.6-1.3 (0.3396), 1.3-0.9 (0.0175) See Figure 3.26.

^{13}C NMR (δ) (integral):178 (0.0061),147-144 (0.1019), 139-137 (0.0080), 130-124 (0.6018), 63.2-62.2 (0.0126), 49.9-48.5 (0.0105), 47.7-39.6 (0.2076), 38.6-32.1 (0.0183), 32.6 (0.0115), 25.5 (0.0025), 23.5 (0.0119), 23.2 (0.0119) See Figure 3.28

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M_n}$: 1100 (^{13}C NMR), 1000 (SEC), 1400 (VPO), 1340 (titration)

Molecular Weight $\overline{M_w}$: 1200 (SEC)

Carboxylation ($\overline{M_n}$(^{13}C NMR)/$\overline{M_n}$(titration)) %: 85±10

TLC (Rf): 0.1, 0.5 (dichloromethane)

Elemental analysis (%): C-88.45, H-7.88, O-3.80 (found); (C-88.4, H-7.71, O-3.89 calculated based on 1100 g/mol and 85% carboxylation)

Characterization of telechelomer produced by investigation 3:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5711), 6.1-5.6 (0.0242), 5.3-5.2 (0.0009), 3.7-3.1 (0.0402), 2.6-1.3 (0.3366), 1.27-0.79 (0.0272) see Figure 3.26.

^{13}C NMR (δ) (integral):178 (0.0121),147-144 (0.1054), 139-137 (0.0131), 130-124 (0.6027), 63.2-62.2 (0.0134), 49.9-48.5 (0.0135), 47.7-39.6 (0.1985), 38.6-32.1 (0.0194), 32.6 (0.0122), 29.5 (0.002), 23.5 (0.0129), 15.0 (0.0011) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M_n}$: 1050 (^{13}C NMR), 1100 (SEC), 1100 (VPO), 1070 (titration)

Molecular Weight $\overline{M_w}$: 1200 (SEC)

Carboxylation ($\overline{M_n}$(^{13}C NMR)/$\overline{M_n}$(titration))%: 98 (88-99)

TLC (Rf): 0.1, 0.6 (dichloromethane)

Elemental analysis (%): C-86.75, H-7.81, O-4.38 (found); C-87.8, H-7.69, O-4.51 (calculated based on 1050 g/mol and 98% carboxylation)

Characterization of telechelomer produced by investigation 4:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5667), 6.1-5.6 (0.0293), 5.3-5.2 (0.0012), 3.7-3.1 (0.0404), 2.6-0.9 (0.3612), 0.2-0.1(0.0012) See Figure 3.26.

^{13}C NMR (δ) (integral): 178 (0.0120),147-144 (0.0944), 139-137 (0.0115, 130-124 (0.5951), 63.2-62.2 (0.0157), 49.9-48.5 (0.0138), 47.7-39.6 (0.1905), 38.6-32.1 (0.0143), 32.6 (0.0139), 29.5 (0.002), 23.5 (0.0137), 23 (0.0137) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 900 (^{13}C NMR), 930 (SEC), 970 (titration)

Molecular Weight $\overline{M}_w$: 1000 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration))%: 93 (83-99)

TLC (Rf): 0.1, 0.5 (dichloromethane)

Elemental analysis (%): C-87.12, H-7.71 (found); C-87.3, H-7.6 (calculated based on 900 g/mol and 93% carboxylation)

Synthesis of Polystyrene Telechelomer and Polystyrene Carboxylic Acid under an Argon Atmosphere

Benzene and toluene were extracted with sulfuric acid for removal of thiophene as described by Perrin.[42] The solvents benzene, toluene, and THF were dried with calcium hydride and distilled onto sodium and potassium alloy. The solvents were stored refluxing over the alloy under an argon atmosphere. When needed, a solvent was distilled into a collection bulb and removed via syringe or cannula. Carbon dioxide from Linde (99.998%) was used in the first 2 methods and carbon dioxide (99.999%) purchased from Airco was used for the remaining two methods.

Styrene was fractionally distilled from calcium hydride under vacuum (1 mmHg) and stored over molecular sieves. Dibutylmagnesium (0.85 M in hexane) from Alfa Chemicals, was transferred into the distilling flask by a cannula, and the hexane was removed under vacuum. The flask was backfilled with argon, and the styrene was transferred into the distilling flask via syringe. The styrene was stirred (usually one hour), distilled into a Schlenk tube, and then syringed directly from the Schlenk tube into the reaction.

Argon methods 1 and 3 were used to synthesize both the polystyrene telechelomer and the polystyrene carboxylic acid. The procedures differed

only in the type of initiator used; n-butyllithium produced the polystyrene carboxylic acid, and 3,5-dioxa-8-lithio-4-methyloctane produced the polystyrene telechelomer.

Argon Method 1 (Ar1)

The reaction vessel was a 500 ml flask equipped with a sidearm stopcock. The reaction flask was flame dried repeatedly under vacuum, then purged with argon, and flame dried again under vacuum. Then the vacuum was partially quenched with argon, and then carried to a toluene still where 70 ml of toluene was transferred by cannula from the collecting bulb of a still. Then the flask was filled with argon, and styrene was added (180 mmol). The system was cooled by a dry-ice/isopropanol bath at -78°C bath, and a small amount of polystyryllithium anion solution (made by adding 2 mmol n-butyllithium to 7 mmol styrene in 50 ml toluene) was added until a yellow-orange polystyryllithium anion color persisted for 30 minutes. A THF solution of either 3,5-dioxa-8-lithio-4-methyloctane (30 ml, 18 mmol) or n-butyllithium (30 ml, 18 mmol) was cooled to -78°C and added by syringe. Then the reactions were warmed to 0°C and left for 30 minutes. The argon was pumped out and replaced with carbon dioxide at just above one atmosphere.

The product was stirred with an equal volume of 1N HCl in methanol for one hour, precipitated in 500 ml of methanol and dried in a vacuum oven at room temperature. The methanol used to precipitate the polystyrene telechelomer was reduced to approximately 100 ml by rotary evaporation, brought to pH 2 with concentrated HCl, and extracted three times with 100 ml of dichloromethane. The dichloromethane extractions were combined, dried with magnesium sulfate, and reduced by rotary evaporation.

Characterization of the polystyrene telechelomer:

^{1}H NMR (δ) (integral) : 7.6-6.4 (0.6293), 4.5-4.3 (0.0004), 3.7-3.1 (0.0402), 2.6-0.9 (0.3457) See Figure 3.26.

^{13}C NMR (δ): 147-144, 137, 129-124, 62.8, 47.7-39.6 See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030(m) See Figure 3.28.

Molecular Weight $\overline{M}_n$: 12,000 (SEC)

Molecular Weight $\overline{M}_w$: 18,000 (SEC)

Characterization of the low molecular weight carboxylic acids extracted from product:

^{13}C NMR (δ): 178 (C=O), 173 (C=O), 169 (C=O), 68.6, 67.5, 67.1, 62.9 (O-CH_2), 45.7, 34.6 (CH-COOH), 27,8, 26.2, 24.5 (O-CH_2-CH_2), 22.1

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1780 (s, C=O stretch), 1260, 1180, 1050 (s, C-O stretches)

Characterization of polystyrene carboxylic acid:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5742), 3.8-3.7 (0.0039), 2.6-0.9 (0.3814), 1.05-0.80 (CH_3, 0.0405) See Figure 3.26.

^{13}C NMR (δ): 147-144, 138, 129-124, 68, 48-38, 33.0 (CH_2-CH_2-CH_2-CH_3), 27.0 (CH_2-CH_2-CH_3), 22.5 (CH_2-CH_3),14.0 (CH_3)
See Figure 3.28.

IR (cm^{-1}): 3000-2900 (s, C-H stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m)

Molecular Weight $\overline{M}_n$: 1000 (SEC), 5750 (titration)

Molecular Weight $\overline{M}_w$: 1300 (SEC)

Carboxylation ($\overline{M}_n$(SEC)/$\overline{M}_n$(titration))%: 18

Argon Method 2 (Ar2)

This method is similar to argon method 1, but in this case, the reaction temperature was kept between -10°C to -70°C.

Characterization:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.6035), 3.8-3.7 (0.0026), 3.3-3.0 (0.0063), 2.6-0.9 (0.3694), 0.89-0.79 ($\underline{C}H_3$, 0.0178) See Figure 3.26.

^{13}C NMR (δ) (integral): 147-144 (0.1012), 130-124 (0.6370), 49.9-48.5 (0.0080), 47.7-39.6 (0.2264), 38.6-35.1, 32.0 ($\underline{C}H_2$-CH_2-CH_2-CH_3, 0.0075), 26.5 ($\underline{C}H_2$-CH_2-CH_3, 0.0046), 22.5 ($\underline{C}H_2$-CH_3, 0.0071), 14.0 ($\underline{C}H_3$, 0.0081) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m)

Molecular Weight $\overline{M}_n$: 1870 (^{13}C NMR), 2210 (^{1}H NMR), 2000 (SEC), 2030 (titration)

Molecular Weight $\overline{M}_w$: 2600 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration))%: 93 (83-99)

TLC (Rf): 0.1, 0.9 (dichloromethane)

Elemental analysis (%): C-89.89, H-8.07 (found); C-90.65, H-7.75 (calculated based on 1870 g/mol and 93% carboxylation)

Argon Method 3 (Ar3)

A 500 ml sidearm equipped reaction flask was flame dried under vacuum, purged with argon and flame dried again under vacuum. Then the vacuum was partially reduced with argon, and the flask was carried to a toluene still where 200 ml of benzene was transferred by a cannula from the collecting bulb of a still.

The flask was filled with argon, and inserted into a 0°C bath after which 1 to 5 ml of a polystyryllithium anion solution (made by adding 2 mmol n-butyllithium to 7 mmol styrene in 50 ml toluene) was added by syringe until the yellow-orange polystyryllithium anion color persisted for 10-15 minutes. Styrene was then added (192 mmol) and more polystyryllithium anion solution was added until the yellow color persisted for 10 to 15 minutes. At this point, the solution was frozen into a rapidly stirring slush, and the initiator solution (192 mmol) was syringed all-at-once into the flask. Quickly afterward, THF (440 mmol) was added, and the solution was allowed to warm to room temperature. After 30 minutes, the solution temperature was lowered to 0°C, and the argon was pumped out and replaced with carbon dioxide at a pressure slightly above one atmosphere.

The product was stirred with an equal volume of 1N HCl in methanol for three hours, precipitated in 500 ml of methanol and dried in a vacuum oven at room temperature.

Characterization of polystyrene telechelomer:

^{1}H NMR (δ) (integral) : 7.4-6.4 (0.6097), 4.8-4.7 (0012), 3.9-3.8 (0.0057), 3.6-3.4 (0.0102), 2.6-0.9 (0.3732) See Figure 3.26.

^{13}C NMR (δ) (integral): 147-144 (0.1012), 130-124 (0.6360), 68.4-67.6 (0.0052), 49.9-48.5 (0.0027), 47.7-39.6 (0.2205), 38.6-35.1 (0.0092), 32.0 (0.0057), 26.5 (0.0042), 22.5 (0.0044) See Figure 3.28.

IR (cm-1): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1700 (w, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m)

Molecular Weight $\overline{M}_n$: 2650 (^{13}C NMR), 2200 (SEC), 7990 (titration)

Molecular Weight $\overline{M}_w$: 2970 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration))%: 33±10

TLC (Rf): 0.1, 0.6 (dichloromethane)

Elemental analysis (%): C-89.24, H-7.84 (found); C-91.24, H-7.76 (calculated based on 2650 g/mol and 33% carboxylation)

Characterization of the polystyrene carboxylic acid:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5742), 3.4-3.0 (0.0039), 2.6-1.05 (0.3814), 1.05-0.80 (CH_3,0.0405) See Figure 3.26.

^{13}C NMR (δ) (integral): 147-144 (0.0973), 130-124 (0.6382), 47.7-39.0 (0.1897), 38.6-35.1 (0.0224), 32.0 (CH_2-CH_2-CH_2-CH_3, 0.0144), 26.5 (CH_2-CH_2-CH_3, 0.0117), 22.5 (CH_2-CH_3,0.0148), 14.0 (CH_3,0.0139) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1700 (m, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m)

Molecular Weight $\overline{M}_n$: 1030 (^{13}C NMR), 990 (^{1}H NMR), 970 (SEC), 6280 (titration)

Molecular Weight $\overline{M}_w$: 1100 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration))%: 16±10

TLC (Rf): 0.1, 0.9 (dichloromethane)

Elemental analysis (%): C-90.58, H-8.22 (found); C-91.38, H-8.12 (calculated based on 1030 g/mol and 16% carboxylation)

Argon Method 4 (Ar4)

This method is same as argon method 3 except a carbon dioxide tank from Airco (99.999%) replaced the Linde (99.998%) carbon dioxide used in method 3.

Characterization:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5736), 2.6-1.05 (0.3814), 1.05-0.80 ($\underline{C}H_3$, 0.0451) See Figure 3.26.

^{13}C NMR (δ) (integral): 147-144 (0.0995), 130-124 (0.6344), 50.0-48.4 (0.0045), 47.7-39.0 (0.2018), 38.6-35.1 (0.0084), 32.0 ($\underline{C}H_2$-CH_2-CH_2-CH_3, 0.0137), 26.5 ($\underline{C}H_2$-CH_2-CH_3, 0.0119), 22.5 ($\underline{C}H_2$-CH_3, 0.0127), 14.0 ($\underline{C}H_3$, 0.0130) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1700 (m, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m)

Molecular Weight $\overline{M}_n$: 1070 (^{13}C NMR), 900 (^{1}H NMR), 775 (SEC), 5830 (titration)

Molecular Weight $\overline{M}_w$: 844 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration))%: 18±10

TLC (Rf): 0.1, 0.9 (dichloromethane)

Elemental analysis (%): C-90.64, H-8.26 (found), C-91.30, H-8.16 (calculated based on 1070 g/mol and 18% carboxylation)

Purification of the Polystyrene-10-Telechelomer

Procedure for Polystyrene-10-Telechelomer Precipitation

The telechelomer was purified by precipitating a concentrated solution of telechelomer (15 g) in dichloromethane (100 ml) into a excess of stirring hexane (900 ml). The precipitation was allowed to continue

overnight at -30°C. The hexane was decanted, and the polymer freeze dried from benzene under high vacuum. An example of the utility of the precipitation technique is found in the following section.

Procedure for Complete Removal of the Acetal Protecting Groups

The polystyrene telechelomer used in this procedure was synthesized by high vacuum method 3, investigation 4 and purified by one precipitation as described in the section entitled, "Procedure for Telechelomer Precipitation." Polystyrene telechelomer (7 mmol) and 35 ml of a 75:25 toluene:water mixture were combined in a 100 ml 3 neck flask equipped with an argon inlet and a condenser topped with an argon outlet. After the telechelomer was dissolved, dichloroacetic acid (0.6 mmol) was added. The solution was refluxed for two hours with a slow argon purge which facilitated removal of volatile products. After the solution returned to room temperature, an equal volume of dichloromethane was added, and the solution was washed with deionized water repeatedly until the washings were neutral to pH paper. Then the solvents were removed by rotary evaporation, and the polymer was reprecipitated in hexane as described previously.

Characterization:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5752), 6.4-5.8 (0.0269), 3.7-3.1 (0.0407), 2.6-1.3 (0.3573) See Figure 3.26.

^{13}C NMR (δ) (integral): (seven second delay between acquisitions) 178 (0.0095),147-144 (0.0961), 139-137 (0.0104), 130-124 (0.6181), 63.2-62.2 (0.0152), 49.9-48.5 (0.0165), 47.7-39.6 (0.1994), 38.6-32.1 (0.0087), 32.6 (0.0123), 23.5 (0.0138) See Figure 3.28.

^{13}C NMR (δ) (integral): (ten second delay between acquisitions) 178 (0.0094),147-144 (0.0946), 139-137 (0.0125), 130-124 (0.6036), 63.2-62.2 (0.0149), 49.9-48.5 (0.0152), 47.7-39.6 (0.1996), 38.6-32.1 (0.0192), 32.6 (0.0154), 23.5 (0.0155) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 950 (^{13}C NMR), 1000 (SEC), 930 (titration)

Molecular Weight $\overline{M}_w$: 1100 (SEC)

Carboxylation ($\overline{M}_n$(^{13}C NMR)/$\overline{M}_n$(titration)%:102 (92-99)

TLC (Rf): 0.1, 0.9 (dichloromethane)

Elemental analysis (%): C-86.95, H-7.63 (found); C-86.95, H-8.00 (calculated based on 950 g/mol and 99% carboxylation)

Procedure for Column Chromatography on Polystyrene-10-Telechelomer

Silica gel solid phase (Fisher 200 to 20 Å) was packed into a cyclohexane column 19 cm high and 1.5 cm wide. Nitrogen pressure, regulated by a mercury bubbler, was used to pack the column and decrease elution times. Polystyrene telechelomer (1 gram), produced from method 3, investigation 3, was dissolved in a minimum of 1:1 cyclohexane-dichloromethane. Then, 200 ml of 3:1 cyclohexane-dichloromethane was used as an eluent followed by 100 ml of 1:3 cyclohexane-dichloromethane, 100 ml dichloromethane, 225 ml of 1:1 dichloromethane to methanol, and 100 ml of methanol. The fractions contained an average of 30 ml with the exception of the last two which contained 122 ml and 100 ml. These fractions were analyzed by TLC and like fractions were combined; fractions

10-13 contained only impurity and fractions 18-21 contained only telechelomer.

Characterization of the polystyrene telechelomer:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5684), 6.0-5.5 (0.0292), 3.7-3.0 (0.0435), 2.6-0.8 (0.3589) See Figure 3.26.

^{13}C NMR (δ) (integral):178 (0.0114),147-143 (0.0982), 139-137 (0.0135), 130-124 (0.6132), 63.2-62.2 (0.0161), 50.7-50.1 (0.0029), 49.6-48.6 (0.0162), 47.0-39.2 (0.1909), 38.6-35.1 (0.0103), 32.6 (0.0140), 23.5 (0.0124), 21.3 (0.0009) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1706 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M_n}$: 900 (^{13}C NMR), 900 (titration)

Carboxylation $(\overline{M_n}(^{13}C\ NMR)/\overline{M_n}(titration)$ %:92-99

TLC (Rf): 0.1 (dichloromethane)

Characterization of the polystyrene impurity:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5617), 3.6-3.3 (0.0300), 2.6-1.3 (0.4019), 0.2 (.00064) See Figure 3.26.

^{13}C NMR (δ) (integral): 147-144 (0.1000), 142 (0.0133), 130-124 (0.5993), 63.2-62.2 (0.0182), 47.0-38.6 (0.1923), 38.3-34.7 (0.0260), 33.5 (0.0158), 32.6 (0.0160), 23.4 (0.0145), 0.80 (0.0045) See Figure 3.29.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M_n}$: 790 (^{13}C NMR), 880 (^{1}H NMR)

TLC (Rf): 0.6 (dichloromethane)

Procedure for Freeze Drying

The polymer (1.0-10 grams) was dissolved in a minimum volume of benzene in a 250 ml round bottom flask which was then attached to the high vacuum line via a ground glass joint. The solution was frozen using a liquid nitrogen bath. Then the flask was evacuated, and the liquid nitrogen bath removed. Since the sublimation of the frozen benzene is endothermic, the solid benzene-polymer mixture remained frozen. The polymer was considered dry when the flask warmed to room temperature.

Synthesis of the Polystyrene-10-Telechelomer Methyl Ester.

A 100 ml three neck flask equipped with a reflux condenser, a septum, and an argon inlet was flame dried. Polystyrene telechelomer (5 mmol), produced by high vacuum method 3, investigation 4, was dissolved in 80 ml of dry methanol, distilled from calcium hydride, and 10 ml dry toluene. Concentrated sulfuric acid (26 mmol) was added, and the solution was refluxed under argon for 2 hours. Then, dichloromethane (100 ml) was added, and the product solution was extracted once with distilled water. The solvent was removed under reduced pressure, and the product was freeze dried. Yield of ester was estimated at 90-99% from ^{13}C NMR integrations of the methyl group on the ester (52 ppm) and the carbon alpha to the carboxylic acid (62 ppm).

Characterization:

^{1}H NMR (δ) (integral) : 7.6-6.3 (0.5569), 3.8-3.2 (O-C$\underline{H}_3$, O-C$\underline{H}_2$, C$\underline{H}$-CO0CH_3, 0.0817), 2.6-0.9 (0.3613) See Figure 3.26.

^{13}C NMR (δ) (integral):174 (0.0108),147-143 (0.0990), 140-138 (0.0098, 130-125 (0.6395), 63.2-62.2 (0.0126), 52.3-51.5 (O-$\underline{C}H_3$, 0.0135), 49.9-48.5 (0.0126), 47.7-39.6 (0.1788), 38.6-35.1 (0.0020), 32.6 (0.0112), 23.5 (0.0101) See Figure 3.28.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1734 (s, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 1150 (^{13}C NMR)

Elemental analysis (%): C-86.23 H-7.80 (found); C-88.45, H-7.79 (calculated based on 1150 g/mol and 99% esterification)

Characterization Methods

Molecular Weight Analyses by Titration

This titration procedure is adapted from the procedure of Quirk.[43,44] A typical titration used a 1.008 x 10^{-2} M potassium hydroxide solution which had been standardized by averaging three titrations of a 0.5007 M sulfamic acid solution (standard deviation was 0.35%). Three 20 ml aliquots of the sulfamic acid solution were titrated using a phenolphthalein indicator and the potassium hydroxide solution.

In a typical analysis, approximately 0.4 grams of oligomer, weighed to 4 significant figures and then dissolved in 20 ml of toluene, was titrated to a phenolphthalein endpoint. The procedure was repeated, and the results averaged (standard deviation 0.37%). A number average molecular weight was determined by dividing the mass of the sample by the moles of potassium hydroxide required to reach the phenolphthalein endpoint (95% confidence range ±1.0%).[45]

The method was shown to be accurate by the analysis of 2-phenylbutanoic acid which produced an average result within 1% of the expected value. As the molecular weight of the sample increases, the endpoint becomes more difficult to detect accurately; specifically, the standard deviation of titrations of a 32,000 g/mol sample was 3.3% which resulted in a 95% confidence range of ± 6.6%.

Minimum Detection of the Acetal Functionality by Proton Nuclear Magnetic Resonance

Complete hydrolysis of the acetal functionality is important for successful telechelomer polymerization; consequently, an accurate measure of acetal concentration is needed. A series of solutions were analyzed by NMR to determine the lower detection limit of the Varian-200 MHz NMR used to analyze the telechelomer. Chloroform solutions of 8-chloro-3,5-dioxa-4-methyloctane with molar concentrations of $1x10^{-3}$ M, $5x10^{-4}$ M, $2.5x10^{-4}$ M, and $1.25x10^{-4}$ M were analyzed, and the minimum detected concentration was $2.5x10^{-4}$ M.

The polystyrene-10-telechelomer NMR samples analyzed had a concentration of at least $1.3x10^{-2}$ M; consequently, the fraction of acetal endgroups which may be undetected, expressed as a percentage, is 1.9%. Thus, a telechelomer sample which has no detectable acetal functionality is at least 98% free of acetal functionality.

Quantitative Carbon-13 Nuclear Magnetic Resonance Molecular Weight Determinations

The quantitative carbon-13 analyses were completed on a Varian 200 MHz NMR spectrometer using sample concentrations of at least $1.3x10^{-2}$ M for the polystyrene-10-telechelomer and $6.0x10^{-1}$ M for the polystyrene

carboxylic acid. The quantitative ^{13}C NMR measurements used a seven second delay between pulses and gated decoupling. The T_1 measurements were made using the inversion-recovery method.[46]

The signals integrated to determine molecular weight correspond to the carbon atoms labeled in Figure 2.4. The T_1 of the alpha hydroxyl carbon in the polystyrene telechelomers (labeled A) (Figure 2.4a) is 0.487 seconds, and the T_1 values of the phenyl carbons (labeled B) range from 0.160 to 0.212 seconds. Polystyrene carboxylic acid was also analyzed (Figure 2.4b); the T1 values for methylene carbon labeled D is 0.827 seconds, and the phenyl carbons (labeled C) range from 0.186 seconds to 0.247 seconds.

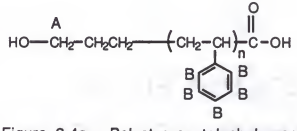


Figure 2.4a. Polystyrene telechelomer.

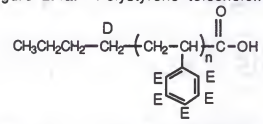


Figure 2.4b. Polystyrene carboxylic acid.

Figure 2.4. Carbon resonances used in quantitative carbon-13 spectroscopy.

The relative areas of phenyl carbons (labeled group B in Figure 2.4a) and alpha hydroxyl carbons (labeled A in Figure 2.4a) are used to calculate the average degree of polymerization ($\overline{X_n}$) using the formula shown in Figure 2.5. The number average molecular weight is calculated from the

average degree of polymerization by multiplying by the molecular weight of styrene and adding the molecular weight of the endgroups. Similarly, the molecular weight of polystyrene carboxylic acid is calculated using the integrals of the resonances labeled D and E in Figure 2.4a.

$$\overline{X_n} = \frac{\text{(integration of group B)}}{\text{(integration of A) x (5)}}$$

Figure 2.5. Formula for calculation of average degree of polymerization.

This method was shown to be accurate by the following experiment. A polystyrene standard purchased from Scientific Polymer Products complete with vapor phase osmometry (VPO) ($\overline{M_n}$=568 g/mole) measurements and viscosity molecular weight measurements was analyzed by carbon-13 NMR, and the molecular weight found was 543 g/mole. The relative error between the molecular weight values is 4.5% (carbon-13 integrations for polystyrene standard methylene at 32 ppm 0.0256; aromatic carbons between 125-129 ppm is 0.5972).

The seven second delay time between pulses was shown to be sufficient by analyzing the same sample once with a seven second delay and again with a ten second delay; the molecular weight determined by both methods agreed within 1% (for integrations of both spectra see the section entitled, "Procedure for Complete Removal of the Acetal Protecting Group").

Molecular Weight Analyses by Vapor Pressure Osmometry (VPO)

Vapor pressure osmometry measures the molecular weight of a sample by comparing the vapor pressure of a series of sample solutions relative to pure solvent. The difference in vapor pressure is compared by measuring

the voltage required to heat a sample cell to an equal vapor pressure as a reference cell. The instrument must be calibrated with a high purity compound of known molecular weight.

The instrument was calibrated with sucrose octaacetate in toluene at 50°C at a current of 20 microamperes. The voltage was measured three times, and an average ΔV was determined for each standard solution (Table 2.1). These values were divided by the concentration of the solution and plotted versus concentration, and the best fit line was extrapolated to zero concentration. Multiplying the intercept by the molecular weight of sucrose octaacetate (678.6 g/mol) yielded a calibration factor K of 2375.

In the same way, the average ΔV was determined for each sample solution (Table 2.1), and the ΔV divided by the concentration was plotted versus concentration. However in this case, the intercept is divided into the calibration factor K to determine the molecular weight of each sample.

Table 2.1. Vapor Pressure Osmometry Data

Sucrose octaacetate standard:

Concentration	ΔV	$\Delta V/C$
10.3	36	3.5
5.15	18	3.5
2.47	8.7	3.5

Intercept is 3.5

High Vacuum Method 3 Investigation 1

Concentration	ΔV	$\Delta V/C$
11.0	14	1.3
5.49	7.2	1.3
2.64	3.5	1.3

Intercept is 1.3

Number average molecular weight is 1800 g/mol.

Table 2.1--continued

High Vacuum Method 3 Investigation 2

Concentration	ΔV	ΔV/C
11.5	20	1.7
5.41	9.5	1.8
3.07	5.3	1.7

Intercept is 1.7

Number average molecular weight is 1400 g/mol.

High Vacuum Method 3 Investigation 3

Concentration	ΔV	ΔV/C
10.7	28	2.1
5.32	18	2.1
2.56	12	2.1

Intercept is 2.1

Number average molecular weight is 1100 g/mol.

Synthesis of Highly Polar Polystyrene

Method 1 (M1)

Polystyrene telechelomer (0.7 mmol), produced by high vacuum method 3, investigation 3, and fractionally distilled titanium tetrabutoxide (Alpha Chemical) (7 x 10^{-4} mmol) were loaded into a polymerization tube[47] which was topped with a three-way stopcock and had a thin capillary tube extending into the flask. The system was heated under vacuum at 205°C for 150 minutes. Then argon was introduced using the three-way stopcock, and 2.5 x 10^{-4} ml of a titanium tetrabutoxide (0.1 gram) and diethyl ether (10 ml) solution was added by syringe through the top of the capillary tube. The capillary was washed with a small amount of diethyl ether. The polymer was then heated to 205°C for 105 minutes under a vacuum of 0.05 mmHg.

Characterization:

^{1}H NMR (δ) (integral) : 7.5-6.3 (0.5926), 4.0-3.4 (0.0267), 3.3-3.0 (0.0110),

2.6-01.1 (0.3494), 1.1-0.66 (0.663), 0.15 (0.0022)

See Figure 3.26.

^{13}C NMR (δ) (integral):173 (0.0153),146-143 (0.1046), 140-138 (0.0149), 129-124 (0.6110), 95.8 (0.0002), 64.8-63.7 (0.0124), 63.2-62.2 (0.0033), 62.1-61.3 (0.0004), 49.9-48.2 (0.0083), 47.7-39.6 (0.1825), 38.6-32.1 (0.0202), 32.6 (0.0025), 28.2 (0.0118), 23.0 (0.0128) See Figure 4.13.

Molecular Weight $\overline{M}_n$: 7000 (SEC), 32,600 (titration)

Molecular Weight $\overline{M}_w$: 12,000 (SEC)

Carboxylation ($\overline{M}_n$(SEC)/$\overline{M}_n$(titration))% 21

Method 2 (M2)

The two experiments completed using this method are similar, the differences being catalyst concentration and amount of telechelomer used initially. One of the experiments used 0.1 mole % of titanium tetrabutoxide (Alpha Chemical) to telechelomer (0.7 mmol), and the other used 0.3 mmol of telechelomer and no catalyst.

Polystyrene telechelomer (0.7 mmol), produced by high vacuum method 3 investigation 3, and fractionally distilled titanium tetrabutoxide ($7x10^{-4}$ mmol, $2.5x10^{-4}$ ml of a solution consisting of 0.1 gram titanium tetrabutoxide and 10 ml diethyl ether) were dissolved in a minimum volume of diethyl ether. The telechelomer and catalyst solution was cast into a film under argon and heated in a vacuum oven at 200°C for 10 hours. Note: the seal on the vacuum oven door was damaged by the high temperature.

Characterization of highly polar polystyrene synthesized with 0.1 mole % titanium tetrabutoxide:

^{13}C NMR (δ) (integral):173 (0.0153),146-143 (0.1046), 140-138 (0.0149), 129-124 (0.6110), 95.8 (0.0002), 64.8-63.7 (0.0124), 63.2-62.2 (0.0033), 62.1-61.3 (0.0004), 49.9-48.2 (0.0083), 47.7-39.6 (0.1825), 38.6-32.1 (0.0202), 32.6 (0.0025), 28.2 (0.0118), 23.0 (0.0128) See Figure 4.13.

Molecular Weight $\overline{M}_n$: 7900 (SEC), greater than 32,600 (titration)

Carboxylation $(\overline{M}_n(SEC)/\overline{M}_n(titration))$% less than 21

Characterization of highly polar polystyrene produced with no catalyst:

^{1}H NMR (δ) (integral) : 7.5-6.3 (0.5930), 4.0-3.4 (0.0245), 3.3-2.9 (0.0130), 2.6-01.1 (0.3502), 1.1-0.66 (0.0193) See Figure 3.26.

IR (cm^{-1}): 3000-2900 (s, C-H stretch), 1725 (s, C=O stretch), 1600, 1490 and 1450 (m, s, s, aromatic C=C stretches), 1220 (m), 1150 (m, ester stretch), 1030 (m, C-O stretch)

Molecular Weight $\overline{M}_n$: 4600 (SEC), 10,100 (titration)

Molecular Weight $\overline{M}_w$: 10,400 (SEC)

Carboxylation $(\overline{M}_n(SEC)/\overline{M}_n(titration))$% 45

Elemental analysis (%): C-87.47, H-7.85, O-2.73 (found); C-89.50, H-7.37, O-3.04. (calculated based on repeat unit)

Investigation of Solution Polycondensation Techniques using Tropic Acid

Triphenylphosphine and Hexachloroethane Activation

The method used followed the procedure of Ogata[48] as closely as possible. Tropic acid (20 mmol) and triphenylphosphine (24 mmol) were dissolved in pyridine (20 ml) and mechanically stirred in a resin kettle. Then hexachloroethane (30 mmol) was added, and the system stirred for

one hour. After reducing the volume of the product solution to 5 ml by rotary evaporation, precipitation of the polymer was attempted by adding the solution to 200 ml of methanol. This methanol solution was then rotary evaporated, and the residue analyzed by size exclusion chromatography.

Molecular Weight (SEC): $\overline{M}_n$=130 g/mol, $\overline{M}_w$=140 g/mol

Triphenylphosphine Dichloride Activation

All liquids were fractionally distilled with the middle fraction collected for used. Triphenylphosphine oxide was recrystallized from diethyl ether and dichloromethane. Tropic acid was used as received from Aldrich Chemical Company.

The procedure of Ogata[49] was followed closely. A resin kettle equipped with a mechanical stirrer, a septum, and an argon inlet was flushed with argon and then charged with triphenylphosphine oxide (32 mmol) in 20 ml of chlorobenzene. To this mixture, a solution of oxalyl chloride (32 mmol) in 10 ml of chlorobenzene was added with stirring. After 2.5 hours, tropic acid was added, and this mixture was heated to reflux temperature (over 15 minutes) and held for 5 minutes. After 30 minutes, the system had cooled to room temperature. At this point, triethylamine (60 mmol) was added, and the system was heated at reflux 1.5 hours. The volume of the product solution was reduced by rotary evaporation and precipitation attempted in methanol. The methanol solution was than rotary evaporated, and the product analyzed by size exclusion chromatography.

Molecular Weight (SEC): $\overline{M}_n$=130 g/mol, $\overline{M}_w$=130 g/mol

Dialkylcarbodiimide Activation

The temperature, solvent, alkylcarbodiimide, and catalyst system used in the experiments are listed in Table 2.2. The molecular weight measurements of the products, determined using size exclusion chromatography, are also listed. Most of the polymers analyzed contained residual monomer which was detected by chromatography but not included in the calculations to determine average molecular weight or distribution.

Cyclohexane, methanol, and pyridine were freshly distilled from calcium hydride. Tetrahydrofuran was freshly distilled from sodium and potassium alloy. Tropic acid, 1,3-dicyclohexylcarbodiimide, and 1,3-diisopropylcarbodiimide were used as received from Aldrich Chemical Company.

Synthesis of 1:1 Complex of p-Toluenesulfonic acid (PTSA) and 4-(Dimethylamino)pyridine (DMAP). The 1:1 PTSA:DMAP complex was synthesized according to the procedure of Stupp[50]. p-Toluenesulfonic acid (63 mmol) was dried overnight using a Dean-Stark distillation with 400 ml benzene as the solvent. The benzene solution was cooled to room temperature; DMAP (63 mmol) was added, and the product immediately precipitated from solution. The solid was recrystallized from 600 ml of dichloroethane and dried in a vacuum oven overnight. Melting point was 174°C (uncorrected as determined on a Thomas Hoover Capillary Melting Point Apparatus).

^{1}H NMR (δ) (integral): 8.1 (multiplet, 1H), 7.4 (multiplet, 1H), 7.1 (multiplet,1H), 6.7 (multiplet,1H), 3.1 (singlet, 6H), 2.3 (s, 3H)

^{13}C NMR (δ): 158, 140, 129, 126, 107, 40 (N-$\underline{C}H_3$), 22 ($\underline{C}H_3$)

Dialkylcarbodiimide Activation Method 1. This method was adapted from the procedure of Belcheva.[51] A 50 ml three neck flask equipped with

Table 2.2 Results of 1,3-dicyclohexylcarbodiimide (DCC) and 1,3-diisopropylcarbodiimide (DiPC) activated polymerizations of tropic acid.

Entry	Solvent[a]	Temp.°C	PTSA[b]	DMAP[b]	$\overline{M}_w$[c]	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[d]	Method[d]	%Yield[e]
1.	toluene/THF[f]	-5 to 10	0.04	----	2000	1700	1.2	1	15
2.	cyclohexane/THF[f,g]	0	0.5	0.5	7500	4400	1.7	2	50
3.	cyclohexane/THF	0	0.5	0.5	4200	2600	1.6	3	30
4.	cyclohexane/THF[h]	0	0.25	0.25	1600	520	3.1	3	0
5.	toluene/THF[f]	50	0.04	----	450	390	1.1	2	0
6.	toluene/THF[f]	25	0.04	----	600	550	1.1	2	0
7.	cyclohexane/THF	-20	0.25	0.25	7500	4300	1.8	3	30
8.	cyclohexane/THF[g]	-20	0.5	0.5	8000	1300	6.0	3	30
9.	cyclohexane/THF[h]	25	0.04	----	1000	880	1.1	2	0
10.	cyclohexane/THF[h]	50	0.04	----	570	500	1.1	2	0
11.	dichloromethane[f,g]	0	0.5	0.5	260	250	1.2	2	0
12.	cyclohexane/THF	0	0.25	0.25	760	530	1.4	2	0

Note: Unless otherwise specified, each experiment used one and a half equivalents of DCC with respect to monomer. [a]toluene/THF=cyclohexane/THF=5 ml/2 ml. [b]units are equivalents with respect to monomer. [c]from size exclusion chromatography using polystyrene calibration. [d]experimental method see text in this section. [e]yields of polymer which precipitated in methanol, i.e. if no polymer precipitated, then the yeild was recorded as 0. [f]pyridine added (0.25 to 0.35 equivalents with respect to monomer). [g]DiPC used in place of DCC (1.5 equivalents) and one to one complex of DMAP and PTSA used. [h]one to one complex of DMAP and PTSA used

a magnetic stirrer and an argon inlet was charged with tropic acid (6.8 mmol), p-toluenesulfonic acid (0.272 mmol), pyridine (1.7 mmol) and 5 ml of a toluene/THF (5 ml/2 ml) mixture. The mixture was stirred at 50°C for one hour and then cooled to 10°C. At this temperature, 1,3-dicyclohexylcarbodiimide (8 mmol) was added dissolved in 2 ml of the toluene/THF solvent, and the system stirred for 1.5 hours. The mixture was then cooled to -5°C and stirring continued for another 2.5 hours. The mixture was filtered, and the solid washed with dichloromethane. The polymer solution was reduced to a white solid which was redissolved in a minimum of dichloromethane and precipitated into a large excess of methanol. The polymer was recovered by centrifugation and freeze dried from benzene under high vacuum. Quantitative molecular weight determination was completed using the integration of the methylene adjacent to the hydroxyl functionality on the endgroup (64.4 ppm), and the integration of the aromatic carbons between 130 and 127 ppm.

Characterization:

^{1}H NMR (δ) (integral) : 7.4-6.8 (0.6111), 4.7-4.0 (0.2412), 4.0-3.6 (0.1331), 0.153-0.018 (0.0146) See Figure 4.16.

^{13}C NMR (δ) (integral): 174 (0.0055), 170 (0.0848), 136-135 (0.0087), 134-133 (0.1070), 130-127 (0.5761), 65.8-64.7 (0.0995), 64.4 (0.0098), 54.0 (0.0056), 50.7-49.5 (0.1031) See Figure 4.17.

IR (cm^{-1}): 3400 (b, H-0 stretch), 3000-2900 (s, C-H stretch), 1728 (m, C=O stretch), 1600,1490 and 1450 (m, s, s, aromatic C=C stretches), 1300-1100 (s, O-C-O ester stretch), 1030 (m) ^{1}H

Molecular Weight $\overline{M}_n$: 1700 (SEC), 1470 (^{13}C NMR).

Molecular Weight $\overline{M}_w$: 2000 (SEC)

Elemental analysis (%): C-71.71 H-5.59, N-0.0 (found); C-73.00, H-5.45, N-0.0 (calculated for repeat unit $C_9H_8O_2$)

Dialkylcarbodiimide Activation Method 2. The following general procedure was used to investigate the polymerization of tropic acid. The specific temperature, solvent, dialkylcarbodiimide, and catalyst system used in the experiments are listed in Table 2.2. A 50 ml three neck flask equipped with a magnetic stirrer and an argon inlet was flame dried and charged with tropic acid (6.8 mmol), p-toluenesulfonic acid, pyridine, and 5 ml of a solvent mixture. The mixture was stirred at 50°C for one hour and then cooled to polymerization temperature. The dialkylcarbodiimide was added all at once, and the system stirred for 3 to 5 hours. The mixture was then filtered, and the solid washed with dichloromethane. The solution was concentrated and precipitation was attempted in 50 to 200 ml of methanol. If a precipitate formed, then the polymer was recovered by centrifugation, but if no precipitate formed, the methanol solution was concentrated to produce a solid. Size exclusion chromatography was performed without further drying or purification. Before NMR analyses, the polymers were freeze dried from benzene or dried in a vacuum oven at room temperature overnight.

Dialkylcarbodiimides Activation Method 3. This method differs from Method 2 in that a Schlenk tube equipped with a mechanical stirrer was used instead of a three neck flask equipped with a magnetic stirbar.

Nuclear Magnetic Resonance Data from Dialkylcarbodiimide Model Polymerization. Entry 1, Table 2.1:

^{1}H NMR (δ) (integral) : 7.4-6.8 (0.6111), 4.7-4.0 (0.2412), 4.0-3.6 (0.1331), 0.153-0.018 (0.0146) See Figure 4.16.

^{13}C NMR (δ) (integral): 174 (0.0055), 170 (0.0848), 136-135 (0.0087),

134-133 (0.1070), 130-127 (0.5761), 65.8-64.7 (0.0995), 64.4 (0.0098), 54.0 (0.0056), 50.7-49.5 (0.1031). See Figure 4.17.

Entry 2,Table 2.1:

^{1}H NMR (δ) (integral) : 7.4-6.8 (0.5322), 4.7-4.0 (0.2120), 4.0-3.6 (0.1125), 33.3 (0.0061), 2.5 (0.0081), 1.3-0.97 (0.0340). See Figure 4.19.

^{13}C NMR (δ): 170, 134-133, 130-127, 65.8-64.7, 50.7-49.5, 23.($\underline{C}H_3$) See Figure 4.17.

Entry 7, Table 2.1:

^{1}H NMR (δ) (integral) : 7.4-6.8 (0.5874), 4.9-4.0 (0.2344), 4.0-3.6 (0.1161), 2.1-1.6 (ring C$\underline{H}_2$, 0.0914), 1.3-0.97 (0.0719) See Figure 4.19.

^{13}C NMR (δ): 170, 134-133, 130-127, 65.8-64.7, 50.7-49.5, 42, 25 (ring $\underline{C}H_2$), 24 (ring $\underline{C}H_2$) 22, 21. See Figure 4.17

Entry 12, Table 2.1:

^{1}H NMR (δ) (integral) : 7.4-6.8 (0.4848), 4.6-4.0 (0.2043), 3.9-3.5 (0.1396), 3.4 (0.0628), 2.0-1.4 (ring C$\underline{H}_2$, 0.0927). See Figure 4.19.

^{13}C NMR (δ): 170, 134, 130-127, 75, 65.8-64.7, 50.7-49.5, 42, 25 (ring $\underline{C}H_2$), 24 (ring $\underline{C}H_2$). See Figure 4.17.

CHAPTER 3
SYNTHESIS OF THE POLYSTYRENE TELECHELOMER

The objective of this dissertation is to describe the synthesis of polystyrene with regularly spaced ester functional groups in the backbone of the polymer. Control of the spacing between the ester groups requires a unique strategy which uses polystyrene-10-telechelomer **(9)** (Figure 3.1) as a monomer in a condensation polymerization that in turn forms highly polar polystyrene **(13)**. This chapter discusses the synthesis and characterization of the polystyrene-10-telechelomer **(9)**.

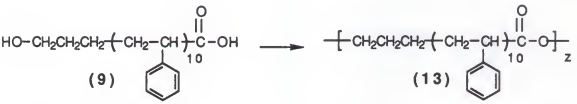


Figure 3.1. Polycondensation of the polystyrene-10-telechelomer **(9)** leading to highly polar polystyrene **(13)**.

A polystyrene-10-telechelomer can be described as an oligomer of polystyrene which has approximately 10 styrene repeat units and is perfectly functionalized on each end. A "telechelomer," a new term derived from the words "telechelic" and "monomer," describes an oligomer capable of forming a high polymer via step polymerization with itself.[52] In this case, polystyrene is functionalized with hydroxy and carboxylic acid endgroups.

The synthesis of a polystyrene telechelomer is shown schematically in Figure 3.2. A compound bearing a protected alcohol group **(10)** initiates anionic oligomerization of styrene to form a polystyryllithium anion **(14)** which reacts with carbon dioxide to produce a carboxylate salt **(15)**. This salt is protonated, and the protecting group on the initiator is removed to produce a polystyrene telechelomer **(7)**.

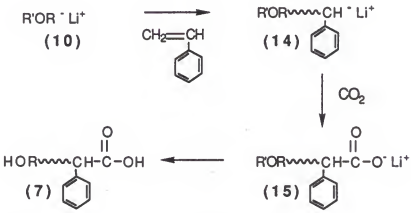


Figure 3.2. Schematic of polystyrene telechelomer **(7)** synthesis.

Factors Affecting Telechelomer Synthesis

The length of the polystyrene spacer between ester functionalities in highly polar polystyrene is determined by the chain length of the polystyrene telechelomer itself. For example, a telechelomer with an average chain length of ten styrene repeat units condenses into a polymer with an average of ten styrene repeat units between each ester, and a telechelomer with a narrow chain length distribution ($\overline{M_w}/\overline{M_n}$=1.1) ensures a nearly uniform spacing of ester groups in the polymer.

Since the polymerization of the telechelomer proceeds by a step propagation mechanism, a high molecular weight polymer cannot be

attained unless 98% of the telechelomer chain ends combine to form esters.[53] This high conversion can only be achieved if the telechelomer is completely functionalized. Thus, high endgroup purity is another requirement in the synthesis of telechelomers.

These requirements for synthesizing telechelomer can be satisfied by using living anionic polymerization, a synthetic method that offers control over chain length, distribution of chain lengths, and high endgroup functionalization.[54-56] However, chain length and distribution are controlled only if the initiation step of the mechanism is faster than the propagation step.[54,55] In the case of the research described herein, the initiation reaction is a nucleophilic attack of an alkyllithium compound on styrene, forming a resonance-stabilized styryllithium **(16)** (Figure 3.3a). Propagation begins when the styryllithium reacts with additional styrene monomers to form a polystyryllithium **(17)**, as shown in Figure 3.3b.

Figure 3.3a.

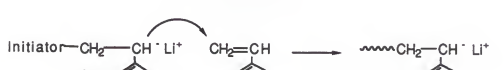


Figure 3.3b.

Figure 3.3. Initiation and propagation of styrene using anionic polymerization.
a) Initiation of anionic styrene polymerization.
b) Propagation of anionic styrene polymerization.

If the initiation stage is largely completed before the propagation begins, then virtually all of the chains propagate at the same time and exhaust the monomer supply simultaneously. The polymer which results has a narrow distribution of chain lengths, and an average chain length dictated by the ratio of the monomer to the initiator.

Living anionic polymerizations have no inherent termination reactions.[55] Consequently, an anionic polymerization proceeds until the monomer concentration is depleted, and the chain ends remain active unless a reagent is added to react with the anion. Any molecule with a labile proton (i.e. water) or an electrophilic site (i.e. carbon dioxide) terminates an anionic polymerization of styrene. The reaction of water with the polystyryllithium **(17)** produces a methylene endgroup **(18)** as shown in Figure 3.4.

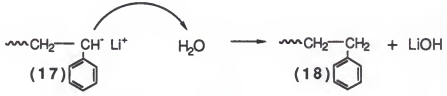


Figure 3.4. Termination of anionic polymerization.

While there are no inherent termination reactions in living anionic polymerizations, extraneous terminating agents, such as oxygen, water, and contaminants in reagents and solvents, can terminate the chains. Water and the reagent contaminants are usually removed by drying agents through repeated vacuum distillation. The exclusion of oxygen and atmospheric moisture demands the use of air sensitive techniques such as Schlenk or high vacuum methods.

The elimination of extraneous termination reactions allows the synthesis of polymers with functional endgroups.[56] Since no impurities are present, an electrophilic reagent can react to form a functional group by terminating every chain end. As an example, carbon dioxide reacts with polystyryllithium **(17)** to form the lithium carboxylate salt at a chain end **(19)** (Figure 3.5).

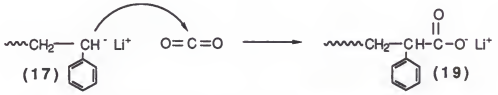


Figure 3.5. Functionalization of chain end by carbon dioxide.

The distribution of the chain lengths increases if extraneous termination reactions are present.[55] The distribution broadens because impurities terminate a fraction of the propagating chains prematurely, which increases the concentration of styrene available for reaction with the remaining propagating chains.

Strategy for the Synthesis of a Polystyrene Telechelomer

The synthesis of the polystyrene-10-telechelomer begins with the creation of an acetal functionalized alkyllithium compound, 3,5-dioxa-8-lithio-4-methyloctane, referred to herein as the acetal initiator **(10)**. This compound is used to initiate the anionic oligomerization of styrene, and consequently, this initiator becomes a chain end **(11)** (Figure 3.6).

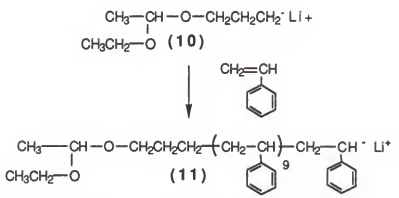


Figure 3.6. Anionic oligomerization with the acetal initiator.

After styrene propagation of the oligomer is complete, the acetal polystyryllithium anions **(11)** are terminated with carbon dioxide (Figure 3.7). The reaction forms a lithium carboxylate salt **(12)** at the chain end which is transformed into the carboxylic acid functionalized endgroup as the acetal functional group is hydrolyzed to the alcohol endgroup. Polystyrene-10-telechelomer **(9)** is then purified by precipitation or column chromatography.

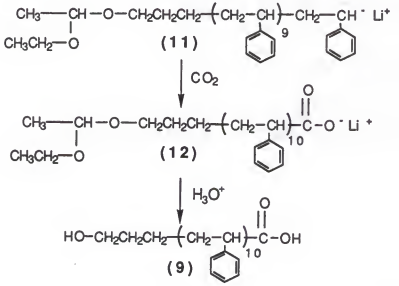


Figure 3.7. Functionalization and hydrolysis forms the polystyrene telechelomer.

The strategy used to produce the polystyrene telechelomer incorporates concepts in the literature of acetal functionalized initiation, anionic oligomerization, and polystyrene carboxylation. These literature investigations are described in the next three sections, "Acetal Initiators," "The Importance of Lewis Bases," and "Endgroup Carboxylation using Carbon Dioxide."

Acetal Initiators

Acetal-containing alkyllithium initiators have been shown previously to be effective in anionic polymerization. In 1974, Schulz[57] reported anionic polymerization of 1,3-butadiene **(20)** (Figure 3.8) with 3,5-dioxa-11-lithio-4-methylundecane **(21)**, a polymerization that was terminated with methanol to form an acetal-functionalized polybutadiene. The acetal was hydrolyzed completely to an alcohol-functionalized polybutadiene **(22)**.

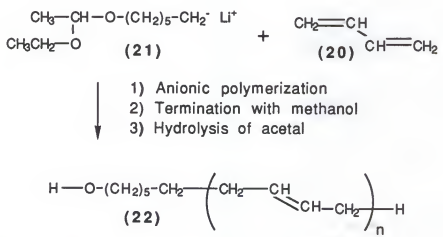


Figure 3.8. A tested acetal initiator, 3,5-dioxa-11-lithio-4-methylundecane **(21)**.

Polybutadiene prepared using this method has high hydroxyl endgroup purity, demonstrating both the inertness of the acetal to anionic polymerization conditions, and the lability of the acetal to hydrolysis. The 3,5-dioxa-11-lithio-4-methylundecane/1,3-butadiene system initiates rapidly as shown by the agreement of the average chain length of the product with the values dictated by the monomer/initiator ratio. In a later publication,[58] the polymerization of styrene is mentioned, but no characterization data or experimental details are reported. This initiator is also effective in the polymerization of hexamethylcyclotrisiloxane (D3).[59]

The initiator used in this dissertation, 3,5-dioxa-8-lithio-4-methyloctane **(10)** (Figure 3.9), was first synthesized by Eaton in 1972 for use in organic synthesis.[39] It is structurally similar to the Schulz initiator **(21)** (Figure 3.9), but has three less methylene units between the acetal functionality and the carbanion (Figure 3.9).

(10) **(21)**

Figure 3.9. The acetal initiator **(10)** used in this research, and the Schulz initiator **(21)**.

In this present study, the acetal initiator **(10)** is used to produce polystyrene telechelomer chains with approximately ten repeat units, and this telechelomer is then used to prepare highly polar polystyrene. Anionic systems designed to produce oligomers are more sensitive to the effects of

slow initiation than anionic systems designed to produce high polymers;[55] consequently, standard anionic polymerization techniques were altered to increase the relative rate of initiation compared to propagation.

Alkyllithium compounds produce systems in which initiation is faster than propagation because the carbanion of the initiator is more reactive than the stabilized carbanion of the propagating anion.[54] As the difference in reactivity between the initiator and the propagating anion increases, so does the relative rate of initiation compared to propagation. This faster relative rate of initiation narrows chain length distribution of the product and enhances control of the average chain length of the product.[54] Thus, approaches which increase the reactivity of the initiator more than the reactivity of the propagating anion are important in this research.

The Importance of Lewis Bases

The addition of a Lewis base enhances the relative rate of initiation to propagation.[60] This increase is caused, at least in part, because Lewis bases activate alkyllithium initiators by making the carbanions more accessible to styrene. Alkyllithium compounds aggregate in non-polar solvents such as benzene, and the addition of a Lewis base such as diethyl ether reduces the size of these aggregates.[60] For example, six n-butyllithium molecules form an aggregate in hexane, while four form an aggregate in a hexane/diethyl ether solvent pair. Stronger Lewis bases, such as tetrahydrofuran (THF) or N,N,N',N'-tetramethylethylenediamine (TMEDA), are expected to reduce the size of the aggregate to an even greater extent.

Allen[61] used THF activation (two equivalents THF were added for every equivalent of n-butyllithium) to synthesize polystyrene oligomers with narrow chain length distributions ($\overline{M}_w/\overline{M}_n$=1.1) and the expected average chain lengths. Similarly, Muroga[62] oligomerized styrene using a THF/toluene (1/9) solvent pair with n-butyllithium initiation at 0°C, and also produced oligomers with the expected average chain lengths and distributions.

One of the factors which influences the relative rate of initiation to propagation is the extent of the interaction between the Lewis base and the lithium aggregate. Quirk[60] determined that the strength of the Lewis base/lithium aggregate interaction is dependent on steric factors by comparing the interaction of the THF **(23)**, 2-methyltetrahydrofuran **(24)**, and 2,4-dimethyltetrahydrofuran **(25)** (Figure 3.10), with the anions, n-butyllithium, sec-butyllithium, and t-butyllithium. The relative strengths of the interactions were determined by measuring the enthalpy of the interaction using calorimetry. Figure 3.10 shows the enthalpy of the

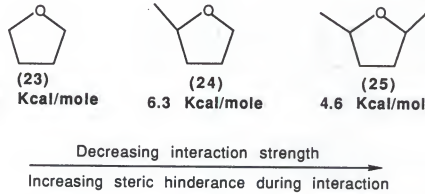


Figure 3.10. Enthalpy of interaction (-ΔH) of substituted THF molecules with n-butyllithium.

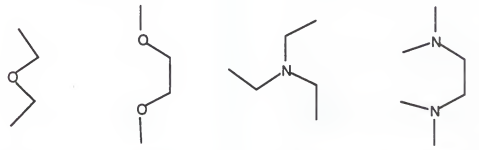
interaction between the substituted THF compounds and n-butyllithium, illustrating that the interaction strength of the bases decreases with the introduction of methyl substituents. The interaction of the substituted THF bases with sec-butyllithium and t-butyllithum produced an identical interaction order; however, sterically hindered t-butyllithium had a relatively weak interaction with all the bases analyzed. For example, the interaction of t-butyllithium with THF is only 0.1 kcal/mole, seventy-five times weaker than the interaction of THF with n-butyllithium.[60]

The number of the alkyllithium molecules in an aggregate also affects the strength of the Lewis base interaction with the alkyllithium,[60] with larger or more branched alkyllithiums forming smaller aggregates. For example, the n-butyllithium aggregate is composed of six molecules while the sec-butyllithium aggregate is composed of four. Table 3.1 shows that the alkyllithium compounds which form the smaller four-molecule aggregates have a stronger interaction with THF, possibly because the alkyllithium is more accessible to the Lewis base (THF).

Table 3.1. The effect of aggregate size on the strength of THF/alkyllithium complex.

Alkyllithium	Size of Aggregate	$-\Delta H$ (Kcal/mole)
C_2H_5Li	6	7.4
$n\text{-}C_4H_9Li$	6	7.5
$(CH_3)_2CHLi$	4	8.5
$(CH_3)_3SiLi$	4	10.3

The bidentate bases, TMEDA **(26)** and 1,2-dimethoxyethane (DME) **(27)** (Figure 3.11), have a stronger interaction with alkyllithium compounds than do the monodentate analogs, diethyl ether **(28)** and triethylamine **(29)**.[60] The TMEDA and DME interactions with n-butyllithium exhibit more than twice the strength of the triethylamine or the diethyl ether interactions. Further, TMEDA has a stronger interaction with n-butyllithium than THF has with n-butyllithium (compare Figure 3.10 and Figure 3.11).



(28) **1.8 Kcal/mole** **(27)** **6.5 Kcal/mole** **(29)** **1.2 Kcal/mole** **(26)** **10.3 Kcal/mole**

Figure 3.11. Interaction enthalpies (-ΔH) of bidentate bases with n-butyllithium.

The same trends affecting the interaction strength of Lewis bases with alkyllithium compounds, i.e. steric and bidentate effects, appear in polystyrene polymerization.[60] Polystyryllithium is the propagating species in the anionic polymerization of styrene; consequently, measuring the interaction of a Lewis base with polystyryllithium supplies information on the role of the Lewis base in the anionic polymerization of styrene.

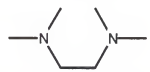
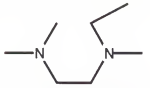
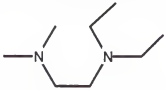
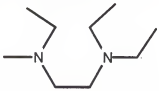
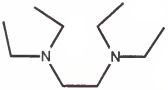
Table 3.2. Enthalpies of interaction of several polystyryllithium/Lewis base complexes.

Lewis Base	-ΔH (kcal/mole)
THF	4.5
2,5-Dimethyltetrahydrofuran	2.3
TMEDA	13.3
Triethylamine	0.3
1,2-Dimethoxyethane	9.8
Diethyl ether	0.3

The interaction of polystyryllithium with THF is stronger than with 2,5-dimethyltetrahydrofuran (Table 3.2), suggesting that the interaction strength depends on the extent of steric interaction in the Lewis base/alkyllithium complex. Similarly, TMEDA and DME have stronger interactions with polystyryllithium than do the monodentate analogs, triethylamine and diethyl ether. Unlike the other Lewis bases analyzed, such as THF, the interaction of TMEDA is stronger with polystyryllithium than with n-butyllithium.

Although the TMEDA interaction with polystyryllithium is stronger than the interaction of THF with the anion, the increase in propagation rate is ten times greater with THF than with TMEDA.[63] This apparent anomaly may be explained by considering the nature of the TMEDA complexed polystyryllithium propagation reaction. The coordinating bidentate TMEDA may sterically hinder the insertion of a styrene monomer and hence produce less of an increase in rate of polymerization than does THF.[64] The hypothesis is supported by comparison of styrene polymerization rates in the presence of a series of TMEDA analogs (Table 3.3);[64] the rate of

Table 3.3. The effect of diamine substituents on polymerization rate.

Diamine	Polymerization Rate of styrene[a]
	300
	230
	145
	80
	40
NO BASE ADDED	30

[a]grams styrene polymerized per gram of n-butyllithium in one hour, data from reference 64.

polymerization decreases as the size of the diamine substituents increases, suggesting that the substituents hinder the reaction of the monomer with the carbanion.

The effects of TMEDA and THF on the anionic oligomerization of styrene continue past the initiation and propagation stages into the termination stage where carbon dioxide reacts with polystyryllithium to form a lithium polystyrene carboxylate salt. The Lewis acids decrease a prevalent side-reaction, ketone formation, by interacting with polystyryllithium and the product carboxylate salt as described in the next section.

Endgroup Carboxylation Using Carbon Dioxide

A living anionic polymerization of styrene can be terminated with carbon dioxide to form a carboxylate salt, which then can be protonated to form a carboxylic acid endgroup (Figure 3.87).[43,44,62,65] While this is the desired reaction, other competing chemistry can occur; for example, the lithium carboxylate salt **(19)** can be attacked by polystyryllithium to form a ketone **(30)** instead (Figure 3.12).[44]

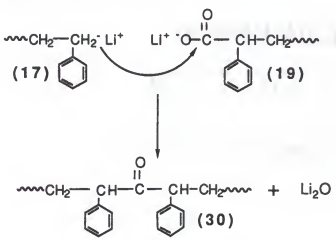


Figure 3.12. Ketone formation competes with carboxylation.

Ketone formation is suppressed by the addition of excess TMEDA or THF before termination with carbon dioxide,[43,44] These Lewis bases may affect the yield of ketone by dispersing polystyryllithium aggregates. Stated differently, the increased distance between a carboxylate salt and the polystyryllithium anion (i.e. less aggregation) may decrease ketone formation.[43]

A further decrease in ketone formation could be caused by coordination of the Lewis base with the lithium cation of the carboxylate salt **(31)** (Figure 3.13). Coordination may weaken the carboxylate anion-cation interaction increasing the electron density of the carboxylate anion, and thereby decreasing the frequency of nucleophilic attack by the polystyryllithium anion.

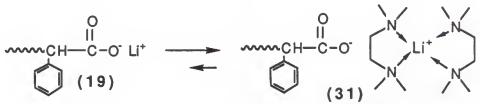


Figure 3.13. TMEDA coordination decreases electrophilicity of the carboxylate anion.

Ketone formation is also decreased if carbon dioxide is allowed to diffuse into an unstirred polystyryllithium solution.[15,16] Saturating the solution with carbon dioxide from the top down ensures a high ratio of carbon dioxide to polystyryllithium, which makes the reaction of the polystyryllithium anion with a polystyrene carboxylate salt less likely.[43]

While THF is used to disrupt alkyllithium aggregation in anionic polymerizations, this Lewis base is known to react with alkyllithium

compounds,[66] and consequently, this Lewis base is not preferred for the chemistry at hand. n-Butyllithium deprotonates THF at the alpha carbon followed by ring opening to form butane, ethylene, and 1-lithio-1-oxapropene **(32)** which upon hydrolysis forms acetaldehyde (Figure 3.14).[66] In a similar way, polystyryllithium could react with THF to form an methylene endgroup.

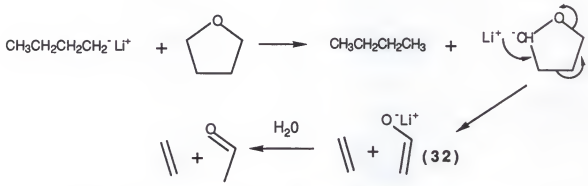


Figure 3.14. Reaction of an alkyllithium with tetrahydrofuran.

Alkyllithium compounds also react with TMEDA by abstracting a proton from a methylene group, which causes subsequent decomposition to lithium dimethylamide **(33)** and N,N-dimethylethenamine **(34)** (Figure 3.15).[67]

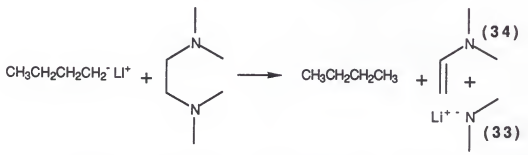


Figure 3.15. Reaction of alkyllithium with TMEDA.

However, TMEDA is more stable to deprotonation by alkyllithium compounds than THF because the protons adjacent to the oxygen atom of THF are more acidic than the protons adjacent to the nitrogen atoms of TMEDA. The greater electronegativity of the oxygen atom, relative to the nitrogen atom, causes the THF protons to be more acidic than the TMEDA protons.

Assimilating the information presented in the first half of this chapter permits the design of a successful synthetic strategy for the preparation of pure telechelomer. The remainder of the chapter describes the preparation of the polystyrene-10-telechelomer.

Implementation of the Telechelomer Synthetic Strategy

These investigations are divided into the four sections to facilitate detailed discussion: preparation of the acetal initiator, anionic oligomerization of styrene, termination with carbon dioxide, and hydrolysis of the acetal polystyrene telechelomer precursor. The remainder of the chapter reports and discusses the results of each section individually.

Preparation of 3,5-dioxa-8-lithio-4-methyloctane, Acetal Initiator

The acetal initiator is prepared by the two step process shown in Figure 3.16. In the first step, a procedure adapted from Eaton[39] is used to synthesize 1-chloro-4,6-dioxa-5-methyloctane **(35)** in good yield by stirring an excess of ethyl vinyl ether with 3-chloropropanol overnight with a catalytic quantity of dichloroacetic acid. The product is pure except for unreacted chloropropanol, which is removed by fractional distillation at reduced pressure.

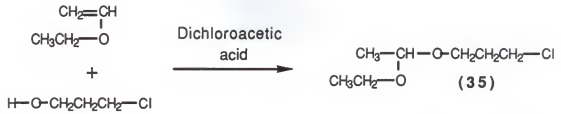


Figure 3.16. Preparation of 1-chloro-4,6-dioxa-5-methyloctane **(27)**.

This compound **(35)** is then metallated with lithium (Figure 3.17); the yield of acetal initiator **(10)** depends on the percentage of sodium alloyed in the lithium metal. Lithium wire alloyed with 1.0% sodium yields 80% product; with less sodium in the alloy (0.1%), only a 10% yield of product is observed. An increase in yield to 90% is achieved by using a lithium dispersion alloyed with 1.0% sodium rather than lithium wire. The most probable cause of the increase in yield is the greater surface area of the lithium dispersion.

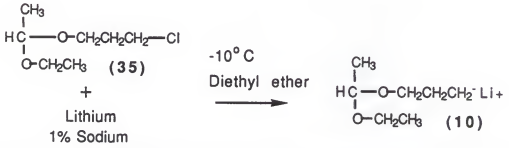


Figure 3.17. Preparation of 3,5-dioxa-8-lithio-4-methyloctane **(10)**.

Anionic Oligomerization of Styrene

In order to further understand the oligomerization of styrene, reactions were done both with the acetal initiator and n-butyllithium; Figure 3.18 shows the chemistry at hand. In most cases, the

oligomerizations were terminated with carbon dioxide and analyzed for chain length and distribution; discussion of the termination reaction is reserved for the section entitled, "Termination with Carbon Dioxide".

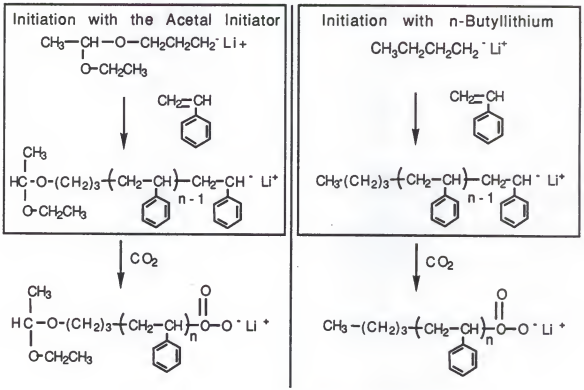


Figure 3.18. Anionic oligomerization of styrene.

High vacuum or Schlenk experimental techniques prevent unnecessary termination reactions, which can broaden chain length distribution.[68] In order to evaluate the utility of these air-sensitive techniques, oligomerizations initiated by n-butyllithium are compared to nearly identical oligomerizations found in the literature.[61,62,43,44]

The n-butyllithium oligomerizations are also used to compare the rate of styrene initiation by the acetal initiator to the rate of styrene initiation

by n-butyllithium. Since the rates of propagation for both initiators can be expected to be similar, the rates of initiation can be compared by analysis of the oligomer chain lengths. Shorter chain lengths are observed for the faster initiator since it produces a greater number of styryllithium anions before the monomer concentration is depleted by the propagating polystyryllithium anions.

Comparison of oligomer degree of polymerizations ($\overline{X_n}$) produced using n-butyllithium ($\overline{X_n}$=51) and the acetal initiator ($\overline{X_n}$=30) in benzene without Lewis acid activation shows that the acetal initiator is a slower initiator than is n-butyllithium (Table 3.4, entries 1 and 2). Since both carbanions produced chain lengths and distributions higher than expected ($\overline{X_n}$=10), two equivalents of THF were added to increase the relative rate of initiation. Again, the acetal initiator produced larger oligomers than expected; however, n-butyllithium initiation with THF activation produced the expected chain lengths and distributions (Table 3.4). Thus, it appears as if

Table 3.4. Anionic oligomerization of styrene using the acetal initiator and n-butyllithium.

Entry	Method[a]	Initiator System	Calc. $\overline{X_n}$[b]	Exp. $\overline{X_n}$[c]	$\overline{M_w}/\overline{M_n}$[d]
1	HV1	Acetal	10	51[d]	1.3
2	HV1	BuLi	10	37[d]	1.2
3	HV3	Acetal/THF	10	14	1.2
4	Ar3	Acetal/THF	10	24	1.4
5	Ar3	BuLi/THF	10	8.9	1.1
6	Ar4	BuLi/THF	10	9.3	1.1

[a]experimental method described in chapter 2. [b]calculated by dividing monomer concentration by initiator concentration. [c]determined by NMR endgroup analysis. [d]determined by size exclusion chromatography.

two equivalents of THF destroys n-butyllithium aggregates which are most likely responsible for high oligomer chain lengths.

The reactivity difference between the acetal initiator and n-butyllithium becomes more pronounced as the reaction temperature is lowered; the acetal initiator produces chain lengths 12 times higher than the values predicted by the monomer-to-initiator ratio, while n-butyllithium initiation again yields the calculated results (Table 3.5).

Table 3.5. Anionic oligomerization of styrene using the acetal initiator and n-butyllithium.

Entry	Method[a]	Initiator System	Calc. $\overline{X_n}$[b]	Exp. $\overline{X_n}$[c]	$\overline{M_w}/\overline{M_n}$[c]
1	Ar1	Acetal/THF	10	120	1.5
2	Ar1	BuLi/THF	10	9.0	1.3

[a]experimental method see chapter 2 [b]calculated by dividing monomer concentration by initiator concentration [c]determined by size exclusion chromatography.

Lower acetal reactivity can be observed visually as the oligomerizations proceed. Even at a lower temperature (-78°C), initiation with n-butyllithium produces the red polystyryllithium solution within 5 minutes, while the acetal initiator produces only an orange solution typical of low polystyryllithium concentration.

Further information suggesting slow initiation by the acetal initiator is provided by the identification of 4-hydroxybutanoic acid (**36**) after carboxylation. This compound can only be formed if the acetal initiator

does not react with styrene throughout the oligomerization but remains active until termination (Figure 3.19).

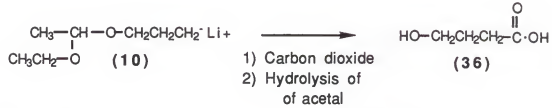


Figure 3.19. The reaction of the acetal initiator with carbon dioxide followed by hydrolysis forms 4-hydroxybutanoic acid **(36)**.

The cause of the decreased reactivity becomes evident by comparing the structures of the acetal initiator and n-butyllithium (Figure 3.20), where the acetal protecting group apparently stabilizes the lithium anion.

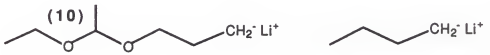


Figure 3.20. The acetal initiator **(11)** and n-butyllithium.

The oxygen atoms of the acetal act as a Lewis base and interact with the lithium cation of the acetal initiator, hindering THF complexation by occupying coordination sites on the lithium cation. The interaction is shown schematically in Figure 3.21 for one molecule of acetal initiator **(10)**, an aggregate of two molecules **(37)**, and an aggregate of four molecules **(38)**. In addition, the interaction of the acetal oxygen atoms may draw the remaining carbon atoms of the acetal group around the

initiator, which could sterically hinder the reaction of the carbanion with styrene and also hinder the complexation with THF.[60] The acetal groups could also interact with lithium cations of other aggregates, increasing overall aggregate size and decreasing the accessibility of the carbanions to styrene or THF. In the future, the acetal initiator could be investigated by nuclear magnetic resonance spectroscopy to determine the extent of the

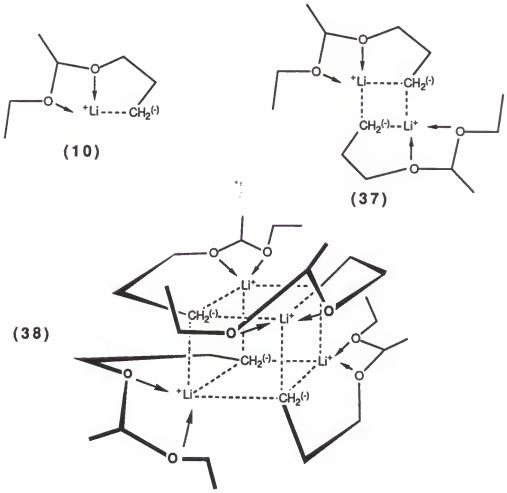


Figure 3.21. Schematic representations of proposed stabilization by oxygen atoms in the acetal initiator **(10)**, the two molecule aggregate **(37)**, and the four molecule aggregate **(38)**. Structure **(38)** is based on crystal structure data of alkyllithium aggregates in the gas phase.[60]

interaction of the oxygen atoms with the lithium atoms and also by viscometric techniques to determine the size of the acetal initiator aggregates in benzene, benzene/THF, and benzene/TMEDA solvent systems.[60,69]

The proposed stabilizing effect of the acetal functionality decreases during propagation as the polystyryllithium chain end moves away from the acetal functionality. This event causes propagation to be faster than the initiation reaction, leading to higher chain lengths and distributions than expected.

This hypothesis suggests that a stronger Lewis base, such as N,N,N',N'-tetramethylethylenediamine (TMEDA), could destabilize these lithium aggregates and negate the effect of the acetal functional group. This Lewis base would also reduce the size of the acetal aggregates and increase the relative rate of initiation. This is exactly what is observed. The acetal initiator with an equimolar concentration of TMEDA at room temperature produces oligomers with a narrow chain length distribution, and the expected chain lengths, as shown in Table 3.6.

Table 3.6. Anionic oligomerization of styrene using TMEDA activation.

Entry	Method[a]	Initiator System	Calc. $\overline{X_n}$[b]	Exp. $\overline{X_n}$[c]	$\overline{M_w}/\overline{M_n}$[d]
1	HV3	Acetal/TMEDA	10	9.5	1.1
2	HV3	Acetal/TMEDA	10	8.0	1.1

[a]experimental methods described in chapter 2 [b]calculated by dividing monomer concentration by initiator concentration [c]determined by NMR endgroup analyses [d]determined by size exclusion chromatography.

These results support the hypothesis that the acetal initiator/TMEDA complex is more reactive than the acetal initiator/THF analog. In addition, the rate of propagation with TMEDA activation is slower than with THF addition;[63] thus, TMEDA addition may both increase the rate of initiation and decrease the rate of propagation compared to THF activation. The combined effects produce a significant increase in the relative rate initiation, compared to propagation, and this increase is responsible for the success of the TMEDA activation technique.

Termination with Carbon Dioxide

While carboxylation (Figure 3.22) would appear to be a simple process, in fact it is not. High carboxylation yields require the complete exclusion of water, oxygen, and impurities which cause premature polystyryllithium termination; in addition, excess THF or TMEDA must be added to prevent a competing reaction--ketone formation. The experimental techniques used for the carboxylation reaction were initially evaluated using polystyryllithium produced by n-butyllithium.

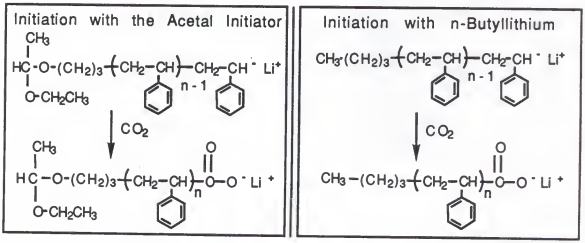


Figure 3.22. Termination of polystyrene oligomers.

The reaction of polystyryllithium with carbon dioxide predominantly forms the carboxylate salt; however, it may also form the ketone **(30)** (Figure 3.23) if a second polystyryllithium anion attacks the carboxylate salt. Ketone formation is inhibited by the addition of 10 to 20 fold excess of TMEDA or THF.[43,44]

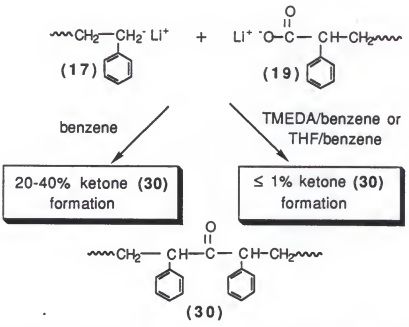


Figure 3.23. The effect of THF and TMEDA on extent of ketone **(30)** formation.

The Lewis bases, THF and TMEDA, are thought to hinder ketone formation by dispersing aggregates.[43,44] In the research described in this dissertation, TMEDA or THF was added to the polystyryllithium anions before termination with gaseous carbon dioxide.

When TMEDA is used to activate the acetal initiator and prevent ketone formation, high yields of carboxylated oligomer are achieved as shown in Table 3.7. The success of these oligomerizations is attributed to the stability of TMEDA to anions.[43]

Table 3.7. Carboxylation using only TMEDA as additive.

Entry	Method[a]	Initiator System	2nd Additive	%COOH[b]
1	HV3	Acetal/TMEDA	TMEDA	98
2	HV3	Acetal/TMEDA	TMEDA	93

[a]described in chapter 2 [b]calculated by dividing number average molecular weight determined by NMR by the number average molecular weight determined by titration as described in chapter 2.

High carboxylation (up to 93%) also is observed using THF if low temperatures are used (-78°C to 0°C)(argon method 3, Chapter 2). However, yields of carboxylated polymer drop substantially if THF is used to activate the alkyllithium initiator at room temperature (Table 3.8). If THF is added during initiation instead of TMEDA, then the percentage of carboxylated chains drops substantially to 66%. However, tetrahydrofuran lowers carboxylation to a lesser extent when added after the majority of the styrene has reacted, as is the case for entry 2 of Table 3.8.

Table 3.8. Comparison of carboxylation yields using THF or TMEDA as additives.

Entry	Method[a]	Initiator System	2nd Additive	%COOH[b]
1	HV3	Acetal/THF	TMEDA	66
2	HV3	Acetal/TMEDA	THF	85

[a]experimental method described in Chapter 2. [b]calculated by dividing number average molecular weight determined by NMR by the number average molecular weight determined by titration as described in chapter 2.

Premature termination of the propagating chains by reaction with THF (Figure 3.24) is the most likely explanation of the lower carboxylation yields produced when THF is used at room temperature. Yields are lowest when THF is added to activate the initiator because the exothermic propagation reaction supplies the activation energy needed for termination by THF.

Figure 3.24. Termination by tetrahydrofuran (THF).

Hydrolysis of the Acetal Polystyrene Telechelomer Precursor

In this stage of the telechelomer synthesis, the carboxylate salt is protonated, and the acetal protecting group is hydrolyzed simultaneously to form the polystyrene-10-telechelomer, as shown in Figure 3.25. The

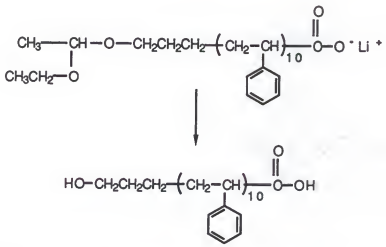


Figure 3.25. Hydrolysis of acetal group and formation of carboxylic acid.

telechelomer is then purified by precipitation or column chromatography, or it can be transformed into the polystyrene-10-telechelomer methyl ester.

Complete removal of the acetal group is accomplished by combining a toluene solution of the telechelomer with a water solution of dichloroacetic acid and refluxing the heterogeneous mixture for six hours. Reflux is essential. At room temperature, residual acetal is detected by nuclear magnetic resonance even after 12 hours. However, either method effectively protonates the lithium carboxylate salt to form the carboxylic acid. The ^1H NMR spectra of acetal polystyrene carboxylic acid and polystyrene-10-telechelomer are shown in Figure 3.26.

The unusually high solubility of the polystyrene-10-telechelomer in methanol provides an opportunity to produce the methyl ester. A one hour reflux with sulfuric acid catalysis produces a 90-99% yield of telechelomer methyl ester (Figure 3.27). This compound is of interest because methyl esters of carboxylic acids are more useful than their acid analogs when polymerized by high temperature melt condensation.[73]

In order to achieve high molecular weights of highly polar polystyrene using step condensation polymerization, the purity of the polystyrene telechelomer must be high.[53] Polystyrene-10-telechelomer was analyzed by thin layer chromatography (TLC) and found to contain a non-polar impurity. As a result, column chromatography or fractional precipitation methods were employed to purify the telechelomer and identify the impurity.

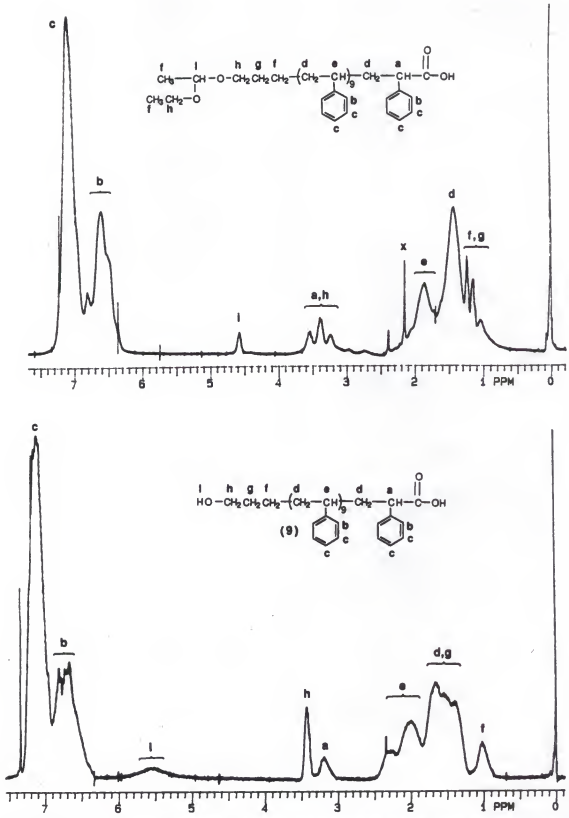


Figure 3.26. ^1H NMR spectra of acetal polystyrene carboxylic acid and the polystyrene-10-telechelomer (**9**). X is residual TMEDA. References for assignments: 70-72.

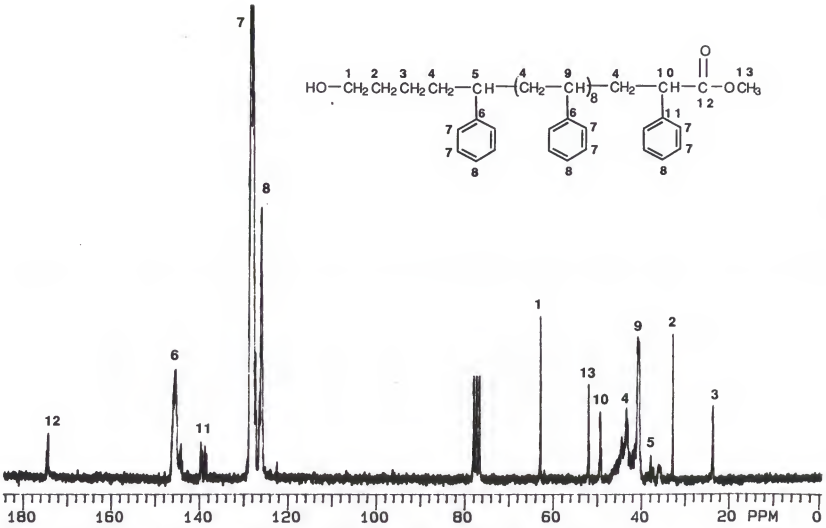


Figure 3.27. ^{13}C NMR spectrum of polystyrene-10-telechelomer methyl ester.
References for assignments: 74-76.

Fractional precipitation increases the carboxylic acid endgroup purity of the telechelomer from 93% to 99% after two precipitations. However, small concentrations of non-polar impurities can still be detected by TLC.

Polystyrene-10-telechelomer, which is free from non-polar impurities, is attained by column chromatography. The integration of quantitative carbon nuclear magnetic resonance signals corresponding to the carbons alpha to the hydroxyl and the carboxylic acid agree within 5%, which suggests equal concentrations of hydroxyl and carboxylic acids (Figure 3.28).

The predominant impurity is isolated by column chromatography, and is identified as polystyrene with a hydroxy endgroup but without a carboxylic acid endgroup. The carbon-13 NMR spectrum of the telechelomer impurity (Figure 3.29) lacks the signals corresponding to the carboxylic acid endgroup (179 ppm and 49.0 ppm) which are present in the spectrum of the polystyrene telechelomer (Figure 3.28). Both these spectra show the resonance of the carbon alpha to the hydroxyl endgroup (62.7 ppm). Similarly, the strong infrared carbonyl absorption at 1706 cm^{-1} present in the polystyrene telechelomer spectrum is absent in the spectrum of the telechelomer impurity, but the absorptions corresponding to the carbon-oxygen single bond are present in both spectra (Figure 3.30).

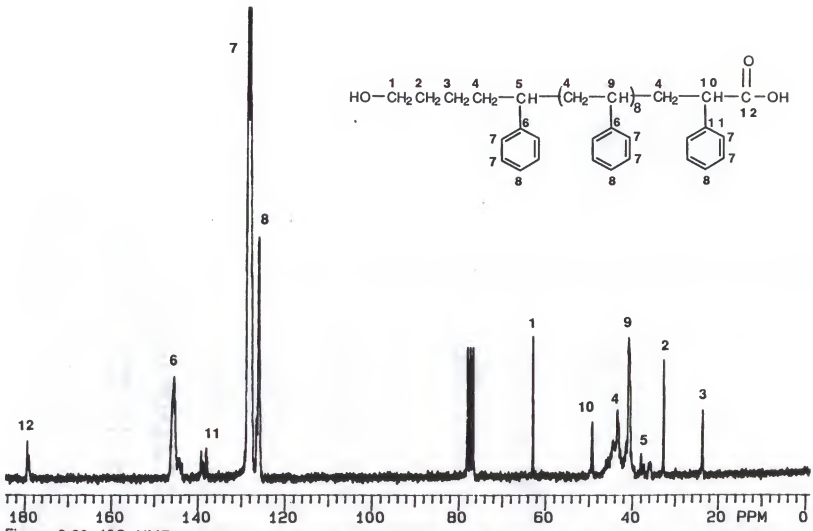


Figure 3.28. ^{13}C NMR spectrum of polystyrene-10-telechelomer. References for assignments: 74-76.

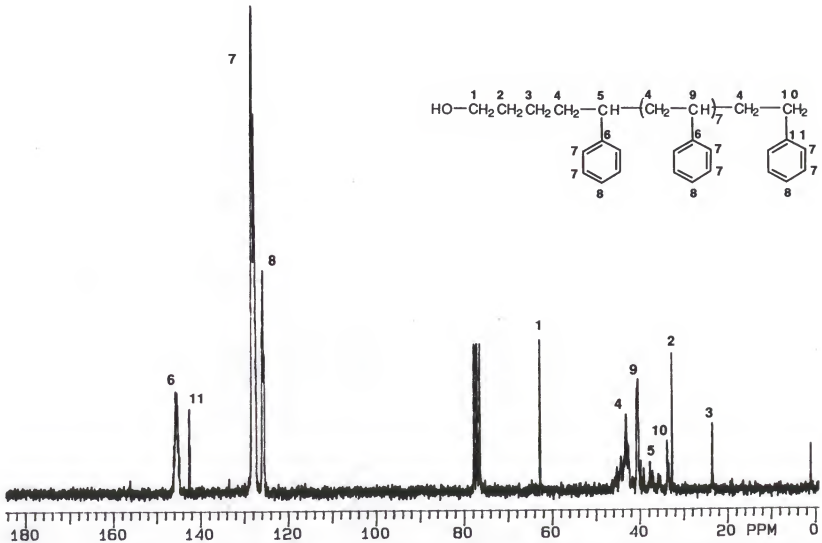


Figure 3.29. ^{13}C NMR spectrum of hydroxyl functionalized polystyrene. References for assignments: 74-76.

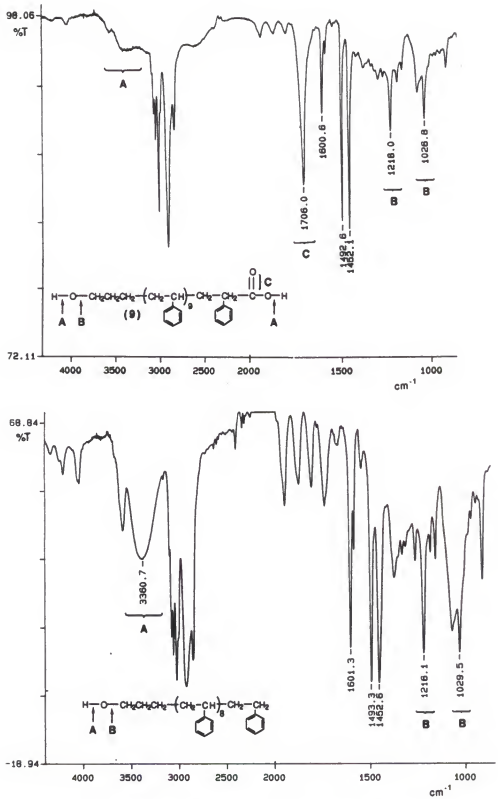


Figure 3.30. Infrared spectra of polystyrene-10-telechelomer (**9**) and hydroxyl functionalized polystyrene. References for assignments: 71, 77.

A probable cause of the formation of hydroxyl functionalized polystyrene impurity is the reaction of polystyryllithium with TMEDA (Figure 3.31). It is possible that this termination reaction could be suppressed by decreasing the polymerization temperature to 0°C, since the rate of the reaction of TMEDA with alkyllithium decreases with temperature.[67] An alternative explanation is termination by water during the oligomerization (Figure 3.4).

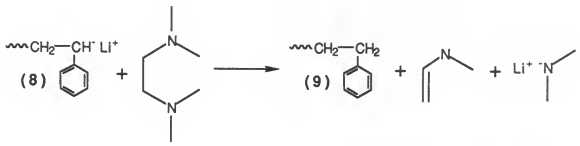


Figure 3.31. Termination by N, N, N', N'-tetramethylethylenediamine (TMEDA).

Identification of the impurity as hydroxyl-terminated polystyrene demonstrates an advantage which is inherent to polymer synthesis with functionalized initiators. The synthesis of polymers with high hydroxyl endgroup purity using functional initiators is possible even if extraneous termination reactions are present in the polymerization (the termination reactions, however, must not initiate a new polymer chain[55]). Table 3.9 reports the results of two oligomerizations where premature termination prevented high carboxylation but did not alter high hydroxy endgroup purity. This point is verified, within experimental error, by comparing vapor phase osmometry (VPO) and quantitative NMR molecular weight data.

Table 3.9 High hydroxyl functionality even with low carboxylic acid functionality.

Entry	Method[a]	VPO ($\overline{X_n}$)	NMR($\overline{X_n}$)	%COOH[b]
1	HV3	12	9.6	85
2	HV3	17	14	66

[a]experimental method described in Chapter 2. [b]calculated by dividing number average molecular weight determined by NMR by the number average molecular weight determined by titration as described in chapter 2.

Vapor phase osmometry measures molecular weight regardless of the nature of the endgroup and NMR determines molecular weight using the hydroxyl endgroup concentration; consequently, agreement of the two molecular weight measurements indicates high hydroxyl functionalization.

The following conclusions can be drawn based on the studies presented in this chapter. The acetal initiator with one equivalent TMEDA in a benzene solvent produces polystyrene oligomers with narrow chain length distribution and average chain lengths corresponding to the value predicted by the monomer/initiator ratio. The acetal initiator without Lewis acid activation or with two equivalents of THF produced chain lengths higher than expected. When compared to n-butyllithium, the acetal initiator was shown to be less reactive toward styrene initiation.

Acetal polystyryllithium can be terminated by carbon dioxide to form the lithium carboxylate in high yield if TMEDA is used to activate the acetal initiator and prevent ketone dimer formation. The addition of THF to the oligomerization system lowers yields of carboxylated chains, if THF is added before the propagation reaction is complete. Lowering the

oligomerization temperature allows the formation of polystyrene carboxylate in high yield even with THF activation.

The acetal polystyrene carboxylic acid salt can be converted quantitatively to the polystyrene-10-telechelomer. The telechelomer is contaminated with hydroxy terminated polystyrene which is removed completely by column chromatography or partially by fractional precipitation. The presence of the hydroxy endgroup in the impurity unequivocally demonstrates that each polystyrene oligomer is functionalized by the acetal initiator. In addition, the methyl ester of the telechelomer can be synthesized in high yield from the polystyrene-10-telechelomer.

With the synthesis of pure polystyrene-10-telechelomer complete, initial investigations into the polymerization of the telechelomer were undertaken. Both high temperature melt polycondensation and low temperature solution polycondensation were investigated and are discussed in the following chapter.

CHAPTER 4

THE FORMATION OF HIGHLY POLAR POLYSTYRENE FROM POLYSTYRENE-10-TELECHELOMER

This chapter discusses the final phase of the chain/step polymerization strategy in which polystyrene-10-telechelomer **(9)**, produced by a chain propagation mechanism, is condensed by a step propagation mechanism. A new breed of polystyrene results, which has regularly spaced ester groups in the main chain **(13)** (Figure 4.1a).

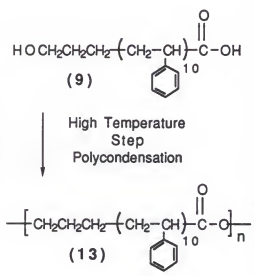


Figure 4.1a

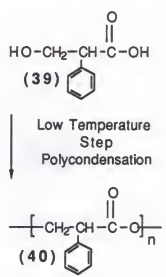


Figure 4.1b

Figure 4.1. Step condensation polymerization
a) High temperature melt techniques produces highly polar polystyrene **(13)**.
b) Low temperature solution techniques are investigated using tropic acid **(39)** in a model study.

Highly polar polystyrene (**13**) is synthesized by melt condensation methods, and a model study using tropic acid (**39**) evaluates low temperature solution condensation methods for future use with the polystyrene telechelomer (Figure 4.1b).

Factors Affecting High and Low Temperature Polycondensation

The condensation polymerizations used in this investigation proceed by a step polymerization mechanism, and as a result, greater than 98% of the polystyrene-10-telechelomer endgroups must combine to attain good yields of high molecular weight, highly polar polystyrene. This type of propagation mechanism first produces short chains which combine to form long chains only at high conversions of endgroups.[78] The relationship between the conversion of endgroups and the average degree of polymerization in step polymerization is described by the Carothers equation (Figure 4.2). As shown in the figure, the average degree of polymerization ($\overline{X_n}$) is two after half of the endgroups react (p=0.5) and increases to 50 only after 98% (p=0.98) of the endgroups combine.[78,79]

As a consequence of the propagation mechanism, the synthesis of high molecular weight, highly polar polystyrene requires perfect stoichiometric balance of monomer reactive groups.[78] For example, polystyrene-10-telechelomer contaminated with 5% hydroxyl endgroup functionalized polystyrene (i.e. does not contain the carboxylic acid endgroup) limits conversion to 95% and the average degree of polymerization to 20 (Figure 4.2).

$$\overline{X_n} = \frac{1}{(1-p)}$$

$$p = \frac{\text{functional groups reacted}}{\text{functional groups initial}}$$

$\overline{X_n}$ = number average degree of polymerization

p	$\overline{X_n}$
0.5	2
0.75	4
0.9	10
0.95	20
0.99	100

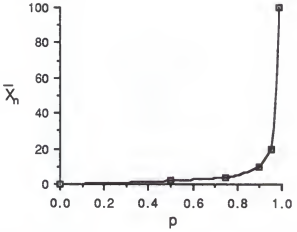


Figure 4.2. The relationship between fraction of reacted endgroups and number average degree of polymerization.

Even with pure monomer, the synthesis of high molecular weight polyester is not guaranteed since the chemistry used to combine the monomers must be free from side reactions and must proceed to quantitative conversions.[78-80] For example, the direct condensation of a carboxylic acid and an alcohol to form an ester fits this requirement (Figure 4.3). Since the reaction is reversible, the formation of high molecular weight polymer requires the removal of the water produced as the ester is formed.[81]

Figure 4.3. Direct condensation of a carboxylic acid and an alcohol.

High temperature melt polycondensation is the classic method for polyester synthesis and is used exclusively in industry.[82,83] A diester or diacid monomer is reacted with a dialcohol monomer in the melt with a catalytic amount of a protonic or Lewis acid to form low molecular weight polyesters. These oligomers are then condensed to high molecular weight using high temperatures and a vacuum. Alternatively, a hydroxy carboxylic acid is used as the only monomer, as described in this dissertation. Polystyrene-10-telechelomer is a hydroxy acid which can be condensed to highly polar polystyrene.

While most polyesters are produced using melt condensation techniques, the high temperatures inherent to the process can lead to polymer chain decomposition.[73] Two chain-scission mechanisms which apply to most polyesters are described in Figure 4.4.

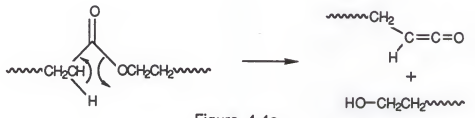


Figure 4.4a

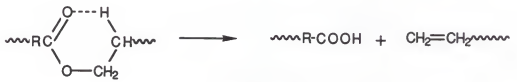


Figure 4.4b

Figure 4.4. Two examples of chain-scission caused by high temperature condensation.

The most prevalent chain-scission mechanism for aliphatic polyesters is cleavage at the acyl-oxygen bond of the ester group, following abstraction of a proton on the carbon alpha to the carboxylic acid. This reaction leads to the formation of ketene and hydroxyl endgroups (Figure 4.4a).[73] Alternatively, the chain-scission produces carboxylic acid and alkene endgroups via the cyclic transition state shown in Figure 4.4b.[73]

High temperature can also lead to decarboxylation of the monomer or the polymer chain end (Figure 4.5).[73] Decarboxylation is a factor for heat sensitive monomers, such as malonic acid; however, substitution of the methyl ester for the carboxylic acid lowers the rate of decarboxylation and enables the synthesis of high molecular weight polymer.[73]

Figure 4.5. High temperature decarboxylation of polymer chain end.

In contrast to high temperature polycondensation, low temperature solution polycondensation is of interest because the chemistry offers a mild synthetic route to highly polar polystyrene. This technique has been applied to heat sensitive monomers such as optically active hydroxy or amino acids.[50,51]

The chemistry originates from the development of activated esterification techniques used widely in organic synthesis.[84-91] Many documented polyesterfication systems lower the activation energy of the reaction by increasing the reactivity of the carboxylic acid itself. Figure 4.6 presents examples of reagents which add to the carboxylic acid to

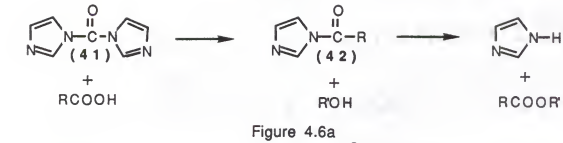


Figure 4.6a

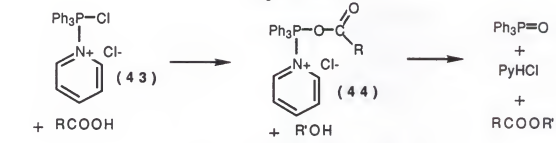


Figure 4.6b

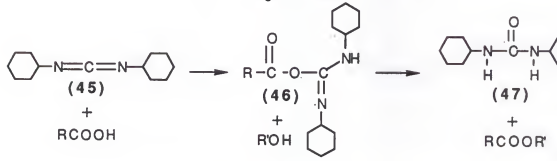


Figure 4.6c

Figure 4.6. Carbonyl activating reagents used in low temperature polyesterfications.
a) Activation by carbonyldiimidazole
b) Activation by triphenylphosphine dichloride and pyridine
c) Activation by 1,3-dicyclohexylcarbodiimide

increase the electrophilicity of the acid. Carbonyldiimidazole **(41)** (Figure 4.6a) activates the acid by forming an N-acylimidazole **(42)**, which when catalyzed by alkoxides, forms polyester.[84,92] Triphenylphosphine dichloride **(43)** in the presence of pyridine reacts with carboxylic acids to produce an acyloxy N-phosphonium salt **(44)** (Figure 4.6b).[48,49,92] The reactive intermediate **(44)** leads to ester, triphenylphosphine oxide, and the pyridine hydrochloride. The activator, 1,3-dicyclohexylcarbodiimide

(DCC) **(45)** (Figure 4.6c) forms an O-acylurea **(46)** which produces an ester and dicyclohexylurea.[84,92-96]

The dialkylcarbodiimides, DCC and 1,3-diisopropylcarbodiimide (DiPC), are reported to be effective activating reagents for the polycondensation of hydroxy carboxylic acids, and therefore, these compounds are particularly well-suited for the polymerization of the polystyrene-10-telechelomer.[50,51] Dialkylcarbodiimides are effective because they react exclusively with the carboxylic acid unlike other activating agents, such as diphenyl chlorophosphate, which may react with the alcohol and thus prevent formation of the ester bond.[50]

Dialkylcarbodiimides have been studied extensively for peptide synthesis,[97] but their use in polyesterification has been hampered until recently by the formation of stable N-acylureas **(48)** (Figure 4.7) which deactivate the carboxylic acid.

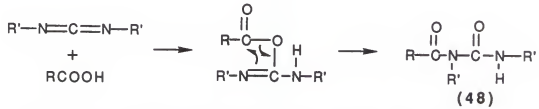


Figure 4.7. N-acylurea formation hinders high molecular weights.

The formation of the N-acylureas **(48)**[93] is inhibited by the addition of protonic acid and nucleophilic base, such as p-toluenesulfonic acid (PTSA) and pyridine or 4-(dimethylamino)pyridine (DMAP).[96,98] Using pyridine and PTSA, Belcheva[51] condensed an aliphatic hydroxy acid into a polymer of 30 repeat units. Higher molecular weight polyester with greater than

50 repeat units was formed from aromatic hydroxy acids and a PTSA and DMAP catalyst pair.[50] In both of these investigations, lower molecular weights are produced if PTSA, DMAP, or pyridine is used individually.

The suppression of N-acylurea formation by PTSA, pyridine, and DMAP is explained by considering the effect of the catalysts on the O-acylurea. The PTSA is thought to hinder the rearrangement to N-acylurea **(48)** by protonation of the O-acylurea **(49)** (Figure 4.8).[96]

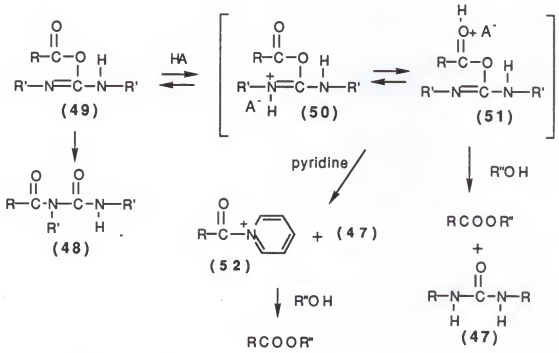


Figure 4.8. Pyridine and p-toluenesulfonic acid (HA) work in tandem to prevent N-acylurea formation.

One of the resulting tautomeric forms **(50)** places the positive charge on the imine nitrogen; the consequent decrease in nucleophilicity of the nitrogen can be expected to hinder the rearrangement to N-acylurea. Alternatively, the O-acylurea can be protonated at the carbonyl oxygen

(51) which increases the electrophilicity of the compound and facilitates the formation of ester directly from the alcohol or indirectly via the acylpyridinium cation **(52)**. Since this cation **(52)** cannot rearrange to N-acylurea, the percentage of N-acylurea formed decreases; however, the rate of reaction also decreases.[93]

Substitution of pyridine by the analogous 4-(dimethylamino)pyridine (DMAP) in acylation reactions is known to increase the rate of the reaction;[99] hence, DMAP can be expected to produce higher reaction rates and lower percentages of N-acylurea than pyridine. The effect of DMAP on polymerization of the aromatic hydroxy acid shown in Figure 4.9 was investigated by Stupp who compared polymer molecular weight produced with and without DMAP catalysis.[50] The addition of DMAP produced a five fold increase in molecular weight of polymer and increased yield of polymer by 30%.

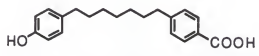


Figure 4.9. Aromatic hydroxy acid used by Stupp.[50]

In contrast to the results of Stupp, DMAP was shown to decrease the molecular weight produced by DCC activation of alpha-(S)-malate (Figure 4.10).[51]

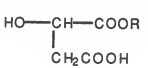


Figure 4.10. Aliphatic hydroxy acid used by Belcheva.[51]

This effect is not without precedent since strong amines such as triethylamine are reported to accelerate the formation of N-acylurea.[93,95] The effect of the base on the mechanism is unknown; however, the strong base may hinder the formation of the protonated O-acylurea **(50** and **51)** (Figure 4.8) which is expected to be less prone to rearrangement to the N-acylurea.[96]

What causes the 4-(dimethylamino)pyridine to produce higher molecular weight polymer in one system, but lower molecular weights in the other? A possible explanation involves the acidity of the carboxylic acid monomers used. The aromatic acid used by Stupp (Figure 4.9) has a pKa of approximately 4.2 (i.e. benzoic acid) while the aliphatic acid used by Belcheva (Figure 4.10) has a pKa of approximately 4.8 (i.e. acetic acid);[100] hence, the greater acidity of the aromatic monomer counteracted the effect of the more basic DMAP.

The molecular weights produced by polyesterification with dialkylcarbodiimide activation are increased by decreasing the polarity of the solvents employed.[50,51,93] Higher polymer molecular weights may be attributed to faster reaction rates and decreased N-acylurea formation in non-polar solvents as shown by an investigation of the DCC activated dehydration of acetic acid in carbon tetrachloride solvent and tetrahydrofuran solvent (Figure 4.11).[93]

Formation of acetic anhydride **(53)** is 34 times faster in carbon tetrachloride than in tetrahydrofuran, and the percentage of N-acetylurea **(54)** produced decreases from 40% in tetrahydrofuran to 0.0% in carbon tetrachloride. The solvent effect is thought to be caused by strong tetrahydrofuran solvation of the carboxylic acid which hinders O-acetylurea **(55)** and anhydride formation by decreasing the

nucleophilicity of the carboxylic acid. The higher percentage of N-acetylurea **(54)** in tetrahydrofuran solvent may result from the lower nucleophilicity of acetic acid. The low reactivity of the acid may increase the lifetime of the O-acetylurea **(55)** so that a higher percentage of these intermediates rearrange into N-acylurea **(54)**.

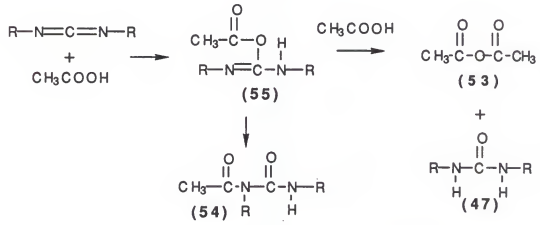


Figure 4.11. Dicyclohexylcarbodiimide assisted dehydration of acetic acid.

The molecular weights of the polymers produced by dialkylcarbodiimide condensations increase with decreasing temperature.[50] The effect can be attributed to decreased N-acylurea formation at lower temperature.[93]

Temperature, solvent polarity, and type and concentrations of catalysts affect the molecular weight produced by dialkylcarbodiimide assisted polycondensation. In this dissertation, a model study is used to examine different conditions in order to facilitate polymerization of the polystyrene-10-telechelomer to highly polar polystyrene.

With the knowledge of melt condensation and solution techniques presented in the first half of this chapter, a strategy was devised to find

an effective experimental technique to polymerize the polystyrene-10-telechelomer. Standard high temperature melt techniques were investigated first since they are the common method of polycondensation.

The Synthesis of Highly Polar Polystyrene

High temperature melt condensation of the polystyrene-10-telechelomer produces highly polar polystyrene. Several variations in technique are described in chapter 2, but in general, the telechelomer is heated to 120°C to 210°C with a titanium tetrabutoxide catalyst under a constant vacuum for several hours (Figure 4.12).

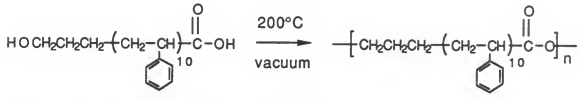


Figure 4.12. High temperature condensation of the polystyrene-10-telechelomer forms highly polar polystyrene.

The transformation of the carboxylic acid and hydroxyl endgroups into the ester functionality of highly polar polystyrene is detected by a shift in the carbonyl ^{13}C NMR resonance from 179 ppm to the expected ester resonance of 174 ppm (Figure 4.13) and also by a shift in the resonance of the carbon alpha to the alcohol from 62.7 ppm to 64.2 ppm (Figure 4.13).[76] Since infrared spectroscopy is also sensitive to the nature of the carbonyl group, the formation of the ester bonds in highly polar polystyrene causes the anticipated decrease in wavelength of absorption from 1706 cm^{-1} to an ester absorption of 1728 cm^{-1} (Figure 4.14).[77]

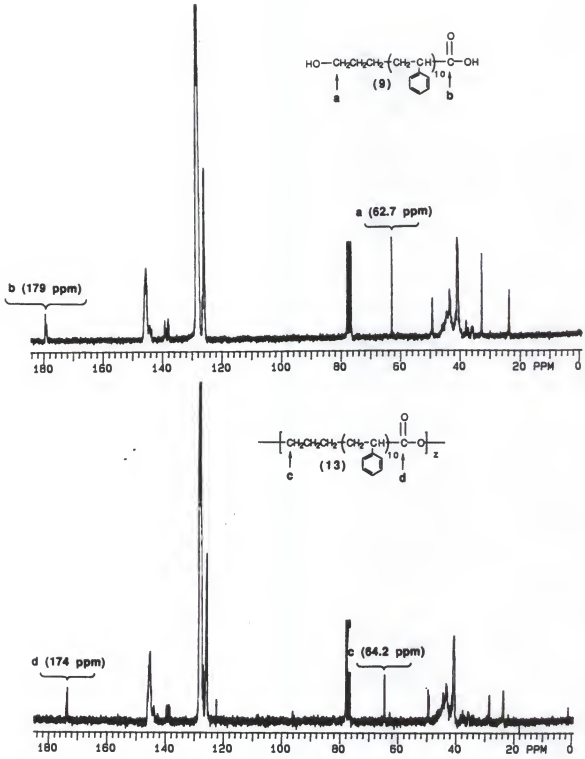


Figure 4.13. ^{13}C NMR spectra of the polystyrene-10-telechelomer (**9**) and highly polar polystyrene (**13**). See Figure 3.28 for the assignments of the unlabled resonances.

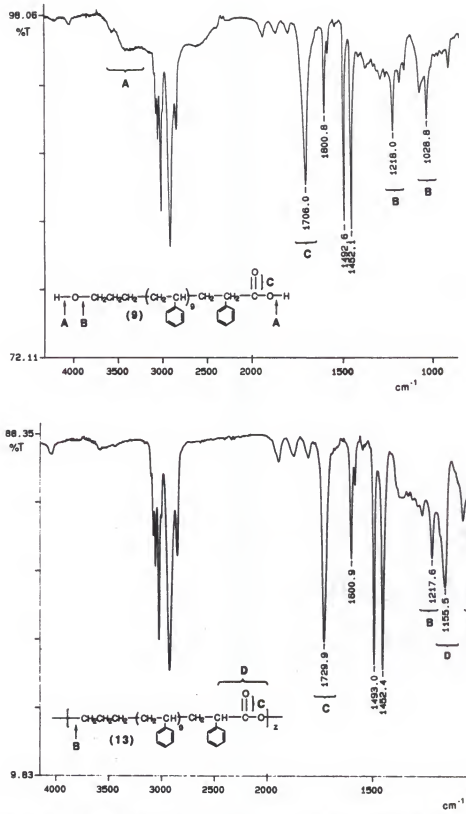


Figure 4.14. Infrared spectra of the polystyrene-10-telechelomer **(9)** and highly polar polystyrene **(13)**. References for assignments: 71, 77.

Ester formation is accompanied by a molecular weight increase which was determined by size exclusion chromatography (SEC) (Table 4.1).

Table 4.1. Highly polar polystyrene molecular weights produced by condensation of the polystyrene-10-telechelomer.

Entry	Method[a]	Ti(mol%)[b]	$\overline{M_n}$(SEC)[c]	$\overline{M_n}$(titration)
1	M1	0.1	7000	32,600
2	M2	----	4600	10,100
3	M3	0.1	7900	>32,600[d]

[a]experimental method used in investigation, see chapter 2. [b]titanium tetrabutoxide catalyst [c]determined by size exclusion chromatography using polystyrene calibration. [d]the titration of entry 3 was attempted but the carboxylic acid endgroup concentration was too low to detect accurately.

The purity of the polystyrene-10-telechelomer used to synthesize highly polar polystyrene was 98%; consequently, complete conversion of endgroups is expected to produce a number average molecular weight ($\overline{M_n}$) of 50,000 g/mol.[78] The maximum $\overline{M_n}$ attained experimentally is 7900 g/mol which corresponds to an 86% conversion of endgroups; thus, 12% of the endgroups were deactivated or left unreacted.

The difference between the number average molecular weights determined by size exclusion chromatography and titration suggests decarboxylation caused the lower than expected conversions (Entries 1-3, Table 4.1). The value calculated by the titration method is dependent on carboxylic acid endgroup concentration, but the SEC values are independent of carboxylic acid; hence, the significantly higher titration values provide

evidence that the percentage (40 to 100 depending on catalyst concentration, Table 4.1) of the endgroups remaining after the polycondensation are not functionalized with a carboxylic acid. The suggested cause is decarboxylation since this reaction is known to occur at high temperatures with carboxylic acid monomers.[73] However, methyl esters of carboxylic acids are reported to be less prone to decarboxylation than the carboxylic acids themselves;[73] therefore, the polymerization of the polystyrene telechelomer methyl ester should be investigated in the future. Since decomposition during melt condensation polymerization was apparent, an investigation of low temperature solution polycondensation techniques was undertaken.

A "Model" Polymerization using Tropic Acid

In order to evaluate both the utility of low temperature polyesterification techniques and optimize reaction conditions with regard to molecular weight of product, a model study of telechelomer polymerization has been conducted using tropic acid **(39)** (3-hydroxy-2-phenylpropanoic acid) as the monomer (Figure 4.15). The alpha phenyl and the primary hydroxyl functionalities of tropic acid provide electronic and steric effects similar to those of the polystyrene telechelomer.

Figure 4.15. Low temperature polycondensation of tropic acid.

Tropic acid was polymerized using several activating systems, and the average molecular weights of the products were determined by size exclusion chromatography. Both number and weight average molecular weights were determined and appear in Chapter 2. This discussion will compare weight average molecular weights since this value is more sensitive to the higher molecular weight fractions.

The first two low temperature condensation systems evaluated used triphenylphosphine dichloride[48,49] as the activating agent and produced oligomers with a weight average molecular weight of less than 200 g/mole. Higher molecular weights were achieved using 1,3-dicyclohexylcarbodiimide (DCC) activation. A polymerization procedure adapted from Belcheva[51] produced poly(tropic acid) with a weight average molecular weight of 2000 g/mol. The identity and molecular weight of the polymer was confirmed by spectroscopic methods (Figures 4.16 and 4.17), and elemental analysis (described in Chapter 2).

As a result of the initial success with DCC activation, dialkylcarbodiimide activation systems were investigated in detail. The molecular weights of the polymers produced by these systems were found to depend on temperature, solvent, plus concentration and identity of catalysts employed.

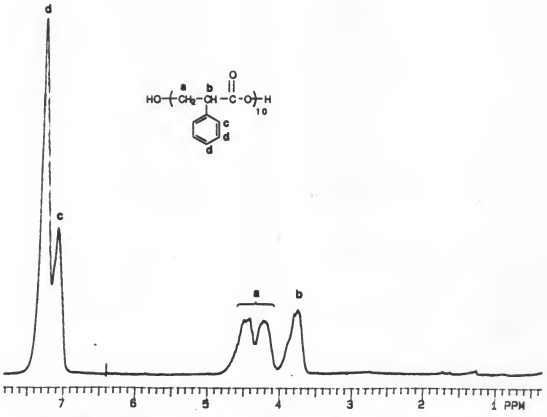


Figure 4.16. ^{1}H NMR spectrum of poly(tropic acid). References for assignments: 73.

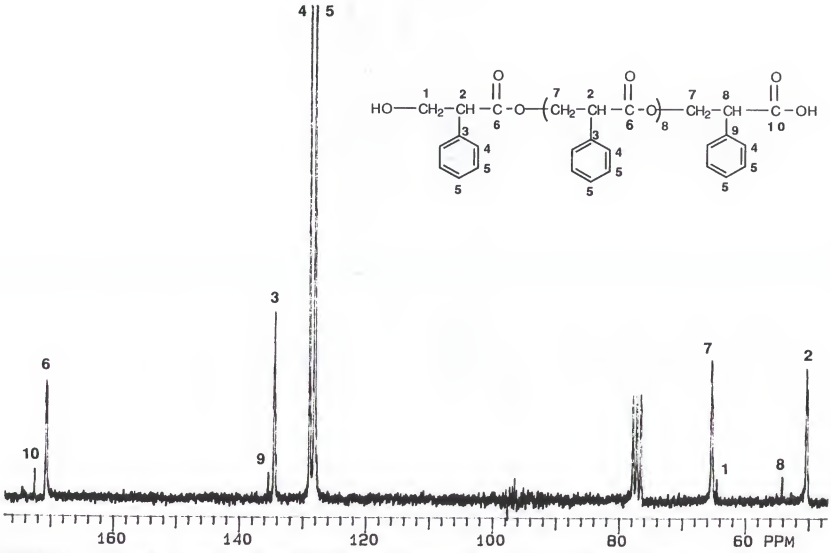


Figure 4.17. ^{13}C NMR spectrum of poly(tropic acid). References for assignments: 74, 76.

The poly(tropic acid) produced using the pyridine and p-toluenesulfonic acid catalyst system of Belcheva has no detectable N-acylurea (48) (Figure 4.7) endgroups; and hence, product molecular weight cannot be limited by N-acylurea formation. The limiting factor is more likely a slow polymerization rate which is dependent on catalyst identity and concentration. Increasing the concentration of p-toluenesulfonic acid (PTSA) and adding 4-(dimethylamino)pyridine (DMAP) (equimolar to PTSA) produces poly(tropic acid) with a significantly higher molecular weight as shown in Table 4.2 (compare entry 1 to entries 2, 3, and 4). However, lower molecular weight polymer was achieved with lower concentrations of catalyst (compare entry 3 to entry 4).

Table 4.2. Effects of p-toluenesulfonic acid and 4-(dimethylamino)pyridine on poly(tropic acid) molecular weight.

Entry	Solvent[a]	Temp.°C	PTSA[b]	DMAP[b]	$\overline{M}_w$
1	toluene/THF[c]	-5 to 10	0.04	----	2000
2	cyclohexane/THF[c,d]	0	0.5	0.5	7500
3	cyclohexane/THF	0	0.5	0.5	4200
4	cyclohexane/THF	0	0.25	0.25	1600

NOTE: DCC used (1.5 equivalents with respect to monomer). [a]toluene/THF=cyclohexane/THF=5ml/2ml. [b]units are equivalents with respect to monomer. [c]pyridine added (0.25 to 0.35 equivalents with respect to monomer). [d]DiPC used in place of DCC and 1:1 DMAP:PTSA complex used.

The increase in poly(tropic acid) molecular weight with 4-(dimethylamino)pyridine addition can be explained by the greater

catalytic ability of 4-(dimethylamino)pyridine compared to pyridine.[101] Both of these bases are thought to nucleophilically attack the protonated O-acylurea **(51)** (Figure 4.18) to form acylpyridinium cations **(56)** which upon reaction with alcohol produce ester; however, the electron donating substituent of 4-(dimethylamino)pyridine increases its nucleophilicity which makes the analog more effective than pyridine.

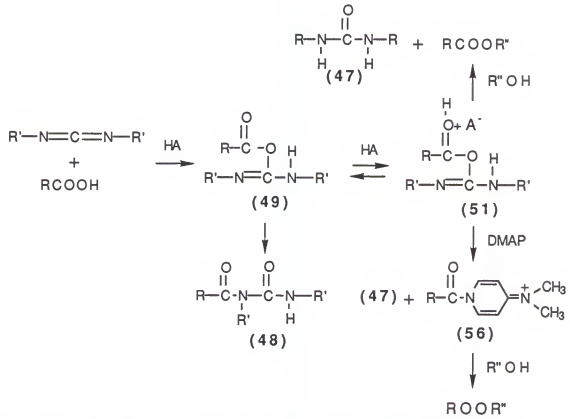


Figure 4.18. Mechanism of ester formation using dialkylcarbodiimide activation with acid and nucleophilic base catalyses.

While higher molecular weight poly(tropic acid) was achieved with a DMAP catalyst concentration of 0.5 equivalents, spectroscopic analyses of the product polymers detected N-acylurea **(11)** formation (Figure 4.19).

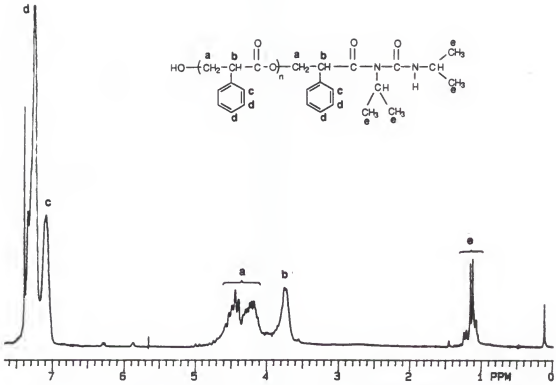


Figure 4.19. ^{1}H NMR spectrum of poly(tropic acid) with an acylurea endgroup. Reference for assignments: 70.

Since strong bases, such as triethylamine, are known to enhance N-acylurea formation, the greater base strength of 4-(dimethylamino)pyridine is suspected to be the cause of the N-acylurea formation.

The increase in N-acylurea formation with DMAP can be used to explain the lower polymer molecular weights achieved at DMAP concentrations of 0.25 equivalents. At higher concentrations of DMAP (0.5 equivalents), the increase in polymerization rate is more significant than the increase in N-acylurea formation; however, at the lower concentrations, the increase in polymerization rate by DMAP is less and N-acylurea formation limits molecular weight.

The proportion of N-acylurea produced compared to O-acylurea decreases with temperature; thus, lower polymerization temperatures can be expected to decrease N-acylurea formation and increase molecular weight. In fact, higher molecular weights are achieved at lower polymerization temperatures; particularly when the reaction temperature is lowered below 0°C as shown by the data in Table 4.3 (compare entries 1, 2, and 3 and compare entry 4 with 5 and compare entry 6 with 7).

Table 4.3. Effect of reaction temperature on molecular weight of tropic acid produced by dialkylcarbodiimide polymerizations.

Entry	Solvent[a]	Temp.°C	PTSA[b]	DMAP[b]	$\overline{M}_w$
1	toluene/THF[c]	50	0.04	----	450
2	toluene/THF[c]	25	0.04	----	600
3	toluene/THF[c]	-5 to 10	0.04	----	2000
4	cyclohexane/THF	0	0.25	0.25	400
5	cyclohexane/THF	-20	0.25	0.25	7500
6	cyclohexane/THF[c,d]	0	0.5	0.5	7500
7	cyclohexane/THF[d]	-20	0.5	0.5	8000

NOTE: DCC used (1.5 equivalents with respect to monomer). [a]toluene/THF=cyclohexane/THF=5ml/2ml. [b]units are equivalents with respect to monomer. [c]pyridine added (0.25 to 0.35 equivalents with respect to monomer). [d]DiPC used in place of DCC and 1:1 DMAP:PTSA complex used.

The polarity of solvent is also known to affect the percentage of N-acylurea formation and the rate of reaction in dialkylcarbodiimide assisted reactions.[57,93] In this study, higher molecular weight polymers are achieved with cyclohexane/THF than with more polar solvents such as toluene/THF or dichloromethane as shown in Table 4.4 (compare entry 1

with 2, entry 3 with 4, and entry 5 with 6 and 7). This trend is confirmed by examination of data published by Belcheva[51] in which higher molecular weight polymers are achieved with a benzene/THF solvent pair than with THF solvent or a DMF/methylene chloride solvent pair.

Table 4.4. The effect of solvent polarity on molecular weight of poly(tropic acid).

Entry	Solvent[a]	Temp.°C	PTSA[b]	DMAP[b]	$\overline{M}_w$
1	toluene/THF[c]	25	0.04	----	600
2	cyclohexane/THF[c]	25	0.04	----	1000
3	toluene/THF[c]	50	0.04	----	450
4	cyclohexane/THF[c]	50	0.04	----	570
5	cyclohexane/THF[c,d]	0	0.5	0.5	7500
6	dichloromethane[c,d]	0	0.5	0.5	240
7	dichloromethane[c,d]	25	0.5	0.5	300

NOTE: DCC used (1.5 equivalents with respect to monomer). [a]toluene/THF=cyclohexane/THF=5ml/2ml. [b]units are equivalents with respect to monomer. [c]pyridine added (0.25 to 0.35 equivalents with respect to monomer). [d]DiPC used in place of DCC and 1:1 DMAP:PTSA complex used.

This model study established several trends which are expected to lead to higher molecular weight highly polar polystyrene when the polystyrene telechelomer is polymerized. Lower temperature (-20°C), lower polarity solvent (cyclohexane/THF), and 0.5 equivalents of 4-(dimethylamino)pyridine and p-toluenesulfonic acid produces higher molecular weight poly(tropic acid). In the future, the effect of various DMAP to PTSA to pyridine ratios should be further investigated since

N-acylurea formation can be suppressed by variation of the acidity of the polymerization system.[50,96,98]

The polycondensation of polystyrene telechelomer has been investigated using melt and solution techniques. Highly polar polystyrene is synthesized using melt techniques but molecular weight is limited by decarboxylation. Low temperature solution polymerization, specifically using dialkylcarbodiimides, is a viable alternative as shown by the successful polymerization of tropic acid. These mild techniques should provide a route to higher molecular weight highly polar polystyrene.

REFERENCES

1. Boundy, R.; Boyer, R. *Styrene: Its Polymers, Copolymers and Derivatives*; Reinhold Publishing: New York,1953; pp 1-15.

2. Boundy, R.; Boyer, R. *Styrene: Its Polymers, Copolymers and Derivatives*; Reinhold Publishing: New York,1953; pp 22-23.

3. Billmeyer, F. *Textbook of Polymer Science*; 3rd ed.; Wiley: New York, 1984; pp 383-387.

4. Boundy, R.; Boyer, R. *Styrene: Its Polymers, Copolymers and Derivatives*; Reinhold Publishing: New York, 1953; Chapters 2-21, pp 28-1259.

5. Odian, G. *Principles of Polymerization*; 2nd ed.; Wiley: New York, 1981; p 200.

6. Seymour R. *Polymer News* 1985, *11*, 231.

7. Elias, Hans-Georg; *Macromolecules 2*, 2nd ed.; Plenum Press; New York, 1984.

8. Leaversuch, R. *Modern Plastics* 1987, *64*(1), 44, 45, 59.

9. Schwartz, R. *Modern Plastics Mid-October Encyclopedia Issue*; 1990,106.

10. Moore, E. In *Encyclopedia of Polymer Science and Engineering* ; Mark, H.; Bikales, N.; Overberger, C.; Menges, G.; Krowschwitz, J., Eds.; Wiley: New York, 1989; Vol. 16; pp 1-246.

11. Brandup, E.; Immergut, E. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; p v-81.

12. Billmeyer, F. *Textbook of Polymer Science*; 3rd ed.; Wiley: New York, 1984; p 7.

13. Boundy, R.; Boyer, R. *Styrene: Its Polymers, Copolymers and Derivatives*; Reinhold Publishing: New York, 1953; p 448.

14. Vollmert, B. *Polymer Chemistry;* Springer-Verlag: New York, 1973; pp 607-628.

15. Odian, G. *Principles of Polymerization*; 2nd ed.; Wiley: New York, 1981; p 29-34.

16. Allcock, H.; Lampe, F. *Contemporary Polymer Chemistry;* 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1990; p 544.

17. Brandup, E.; Immergut, E. *Polymer Handbook;* 3rd ed.; Wiley: New York, 1989; v-17.

18. Brandup, E.; Immergut, E. *Polymer Handbook;* 3rd ed.; Wiley: New York, 1989; v-128.

19. Billmeyer, F. *Textbook of Polymer Science*; 3rd ed.; Wiley: New York, 1984; pp 266-267.

20. Kissin, Y. In *Encyclopedia of Polymer Science and Engineering*; Mark, H.; Bikales, N.; Overberger, C.; Menges, G.; Krowschwitz, T.; Eds.; Wiley: New York, 1989; Vol. 15; pp 763-776.

21. Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* 1955, *77,* 1708.

22. Ishihara, N..; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules,* 1986, *19*, 2464.

23. Lantman, L.; Macknight, W.; Lundberg, R. *Comprehensive Polymer Science;* Pergamon Press: New York, 1989; Vol. 2, pp 755-774.

24. Lundberg, R. In *Encyclopedia of Polymer Science and Engineering* ; Mark, H.; Bikales, N.; Overberger, C.; Menges, G.; Krowschwitz, J., Eds.; Wiley: New York, 1989; Vol. 8, pp 393-404.

25. Makowski, H.; Lundberg, R. In *Ions in Polymers;* Eisenberg, A., Ed.; American Chemical Society: Washington, DC, 1980; pp 21-36.

26. Lundberg, R. In *Encyclopedia of Polymer Science and Engineering* ; Mark, H.; Bikales, N.; Overberger, C.; Menges, G.; Krowschwitz, J.; Eds.; Wiley: New York, 1989; Vol. 8, pp 420-422.

27. Eisenberg, A.; Brockman, N. *J. Polym. Sci., Polym. Physics ED.*; 1985, *23,* 1145.

28. Holloday, L. *Ionic Polymers*; Applied Science Publishers, Ltd.: London, 1975; p 35-46.

29. Bazuin, C.; Eisenberg, A. *J. Chem. ED.* 1981, *58(11)*, pp 938-943.

30. Bailey, W.; Wu, S.; Ni, Z. *Makromol. Chem.* 1982,*183,* 1913.

31. Bailey, W.; Wu, S.; Ni, Z. *Macromolecules* 1982, *115(30),* 711-714.

32. Bailey, W. In *Reactive Oligomers*; Harris, F.; Spinelli, H.;,Eds.; American Chemical Society: Washington, DC, 1985; pp 150-151.

33. Bailey, W.; Chou, T.; Feng, P.; Issari, B.; Kuraginsi, V.; Zhou, L. *J. Macromol. Sci., Polym. Chem. ED.* 1988; *A25(5-7)*; pp 781-789.

34. Billmeyer, F. *Textbook of Polymer Science*; 3rd ed.; Wiley: New York, 1984; p 339.

35. Bannerman, D.; Magat, E. in *Polymer Processes;* Schildknecht, C., Ed.; Wiley: New York, 1956; Chapter 7.

36. Matayabas, J. C., Jr.; *Synthesis and Characterization of Regular Segmented Copolymers of Poly(pivalolactone) and Poly(oxyethylene),* Ph.D Dissertation, University of Florida, 1990.

37. Shoemaker, D.; Garland, C.; Steinfeld, J.; Nibler, J. *Experiments in Physical Chemistry*, 4th ed.; McGraw-Hill: New York, 1981; 596-641.

38. Wayda, A.; Dye, J. *J. Chem. Ed.* 1985, *62*, 356.

39. Eaton, P.; Cooper, G.; Johnson, R.; Mueller, R. *J. Org. Chem.* 1972, *32*(12), 1947.

40. Gilman, H.; Hanbein, H. *J. Amer. Chem. Soc.* 1944, *66,* 1515.

41. Gilman, H.; Hanbein, H. *J. Amer. Chem. Soc.* 1961, *83*, 4089.

42. Perrin, D.; Armarego, W. *Purification of Laboratory Chemicals;* 3rd ed.; Pergamon Press: New York, 1988.

43. Quirk, R.; Yin, J. *Macromolecules* 1989, *20*, 85.

44. Quirk, R.; Chen, W. *Macromol. Chem.* 1982,*183*, 2071.

45. Aikens, D.; Bailey, R.; Moore, J.; Giachino, G.; Tomkins, R. *Principles and Techniques for an Integrated Chemistry Laboratory*; Waveland Press: Prospect Heights, IL; 1984; pp 42-56.

46. Levy, C.; Nelson, G.; *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists;* Wiley: New York, 1972; pp 181-184.

47. Sorenson, W.; Campbell, W. *Preparative Methods of Polymer Chemistry*; 2nd ed.; Wiley: New York, 1968; pp 8-12.

48. Ogata, N.; Yasuda, S.; Wu, G.; Tanaka, H.; Sanui, K. *J. Polym. Sci., Polym. Chem. ED.* 1983, *21*, 2609.

49. Ogata, N.; Kitayama, S.; Sanui, K. *J. Polym. Sci., Polym Chem. ED.* 1984, *22*, 2705.

50. Stupp, S.; Moore, J. *Macromolecules* 1990, *23*, 65.

51. Belcheva, N.; Tsetanov, C.; Panayotov, M.; Lazarova, S. *Makromol. Chem.* 1990, *191*, 213.

52. Goethals, E. *Telechelic Polymers: Synthesis and Applications;* CRC Press, Inc.: Boca Raton, FL, 1989; 197.

53. Odian, G. *Principles of Polymerization*; 2nd ed.; Wiley: New York, 1981; p 89.

54. Szwarc, M. in *Advances in Polymer Science #49;* Springer-Verlag: Berlin, 1983, p 60.

55. Odian G. *Principles of Polymerization*; 2nd ed.; Wiley: New York, 1981; p 372-397.

56. Goethals, E. *Telechelic Polymers: Synthesis and Applications;* CRC Press, Inc.: Boca Raton, FL, 1989; p 34-57.

57. Schulz, D.N.; Halasa, A.F.; Oberster, A.E. *J. Polym. Sci. Polym. Chem.* 1974, *12,* 153-166.

58. Schulz, D.N.; Sanora, J.C.; Willoughby, B.G.; McGrath, N.J. *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis;* American Chemical Society: Washington, DC, 1981; pp 427-440.

59. LeFebure, P.M.; Jerome, R.; Piteyssie, P. *Macromolecules* 1977, *10,* 871.

60. Young, R.; Quirk, R.; Fetters, L.T. In *Advances in Polymer Science #56;* Springer-Verlag: New York, 1984; pp 1-42.

61. Allen, V.; Altares, T.; Wyman, D. *J. Polym. Sci.* 1964, *A-2,* 4533.

62. Muroga, Y.; Tsukahara, Y.; Tsai, H.; Yamashita, Y. *Polym. J.* 1987, *19,* 1033.

63. Kminek, I.; Kaspar, M.; Trekoval, J. *Makromol. Chem.* 1982, *183,* 1755.

64. Langer, A. In *Polyamine-Chelated Alkali Metal Compounds, Advances in Chem. Series 130;* American Chemical Society: Washington, DC, 1974; pp 14-15.

65. Sorenson, W.; Campbell, W. *Preparative Methods of Polymer Chemistry;* 2nd ed.; Wiley: New York, 1968; p 282.

66. Honeycutt, S. *J. Organometallic Chem.* 1971, *24,* 1.

67. Eberhardt, G.; Butte,W. *J. Org. Chem.* 1964, *29,* 2928.

68. Sorenson, W.; Campbell, W. *Preparative Methods of Polymer Chemistry;* 2nd ed.; Wiley: New York, 1968; pp 274-286.

69. Silverstein, B.; Bassler, G.; Morrill, T. *Spectroscopic Identification of Organic Compounds*; 4th ed.; Wiley: New York, 1981; pp 181-278.

70. Silverstein, B.; Bassler, G.; Morrill, T. *Spectroscopic Identification of Organic Compounds;* 4th ed.; Wiley: New York, 1981; pp 181-212.

71. Raby, P.; Hestley, F.; Mobbs, R.; Price, C.; Stubberfield, R. *Eur. Polym. J.* 1987, *23*, 455.

72. Bovey, F.; Filipovich, G.; Tiers, G. *J. Polym. Sci.* 1959, *38,* 73.

73. Pilati, F. In *Comprehensive Polymer Science;* Allen, G.; Bevington, J, Eds.; Pergamon Press, 1989; Vol. 5, p 300-302.

74. Jasse, B.; Laupretre, F.; Monnerie, L. *Makromol. Chem.* 1977, *178*, 1987.

75. Torielli, A. *Macromolecules* 1979, *12*, 252.

76. Silverstein, B.; Bassler, G.; Morrill, T. *Spectroscopic Identification of Organic Compounds*; 4th ed.; Wiley: New York, 1981; pp 213-278.

77. Silverstein, B.; Bassler, G.; Morrill, T. *Spectroscopic Identification of Organic Compounds*; 4th ed.; Wiley: New York, 1981; pp 95-135.

78. Odian, G. *Principles of Polymerization*; 2nd ed.; Wiley: New York, 1981; pp 40-55.

79. Billmeyer, F. *Textbook of Polymer Science*; 3rd ed.; Wiley: New York, 1984; pp 25-48.

80. Bamford, C., Tipper C Eds.*Comprehensive Chemical Kinetics;* Elsevier Scientific Publishing, New York, 1976; Vol. 15, pp 495-531.

81. Sorenson, W.; Campbell, W. *Preparative Methods of Polymer Chemistry;* 2nd ed.; Wiley: New York, 1968; pp 130-150.

82. Pilati, F. In *Comprehensive Polymer Science;* Allen, G.; Bevington, J.eds.; Pergamon Press; New York, 1989; Vol. 5, pp 279-285.

83. Moncrieff, R. *Man-Made Fibers*; 5th ed.; Wiley: New York,1970; pp400-439.

84. March, J. *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure*; 3rd ed.; Wiley: New York, 1985; pp 348-351.

85. Haslam, E. *Tetrahedron* 1980, *36,* 2409.

86. Fukumoto, T.; Oka, K.; Nakao, R. *Bull. Chem. Soc. Jpn.* 1981, *54,* 1267.

87. Makaiyama, T. *Agnew Chemie. Int. Ed. Engl.* 1979,*18,* 707.

88. Paul, J.; Adams, J.; Lewis, J. *Synthesis* 1982,429,

89. Hassner, A.; Alexanian, V. *Tetrahedron Lett.* 1978,4475.

90. Ohan, T.; Brook, M. *Synthesis* 1983, 201.

91. Piago-Meseguer, J.; Palomo-Coll, A. *Synthesis* 1980, 547.

92. Pilati, F.; In *Comprehensive Polymer Science;* Allen, G.; Bevington, J.eds.; Pergamon Press 1989; Vol. 5, pp 285-290.

93. Mikolajczyk, M.; Mikielbasinski, P. *Tetrahedron* 1981, *37,* 233.

94. Silverstein, R.; Detar, D. *J. Am. Chem. Soc.* 1966, *88,* 1013.

95. Silverstein, R.; Detar, D. *J. Am. Chem. Soc.* 1966, *88,* 1020.

96. Holmberg, K.; Hansen, B. *Acta Chem. Scand. B.* 1979, *33,* 410.

97. Singh, J. *Peptides* 1979, *1*, 241.

98. Boden, E.; Keck, G. *J. Org. Chem.* 1985, *50*, 2394.

99. Carey, F.; Sundberg, J. *Advanced Organic Chemistry Part B: Reactions and Synthesis*; Plenum Press: New York, 1983; pp 121-122.

100. Pine, S. Hendrickson, T.; Cram, D.; Hammond, G. *Organic Chemistry, 4th ed.*: McGraw-Hill: New York, 1980; pp 199-202.

101. Odian, G. *Principles of Polymerization*; 2nd ed.; Wiley: New York, 1981; pp 20-25..

BIOGRAPHICAL SKETCH

Jeffrey G. Linert was born on December 18, 1963, in Downers Grove, Illinois. He began his undergraduate work in 1981 at the University of Iowa at Iowa City and received his Bachelor of Science degree in chemistry in 1986. In the fall of that same year, Jeff began graduate work at the University of Florida, where he studied under Dr. Kenneth Wagener. He received his Ph.D. in polymer chemistry in 1991 and began a career in industry with the 3M Company, in St. Paul, Minnesota.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Wagener, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Charles Beatty
Professor of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James Boncella
Assistant Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dean, Graduate School

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